

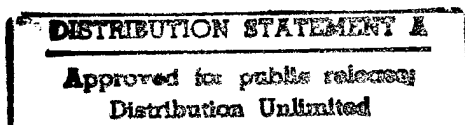
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UDC 53.087.9:54-138

Sensor To Measure Aerosol Charges

917M0010E Moscow *KHIMICHESKOYE I
NEFTYANOYE MASHINOSTROYENIYE in Russian*
No 9, Sep 90 p 11

[Article by V. A. Ivanov and L. P. Baranov]

[Abstract] The aerosol charge-measuring sensor described in this article is intended to increased the operating efficiency of devices based on electron-ion technology. The sensor's operation is based on the precipitation of particles of a solid or liquid disperse phase from a gaseous medium and isolation of an electric signal in an insulated Faraday cylinder. When a particle charge is measured, the packing for the entire Faraday

cylinder is kept constant at 1.8 g per cylinder or 0.36 g/cm³ working volume. Having this packing mass when dust-bearing gases are sucked through the cylinders (at a flow rate of 20 l/min or 1.3m³/h) provides an identical air drag, 3,500-4,000 Pa. When this is the case, the coefficient of dust particle breakthrough does not exceed 1.8-2.1%. An electrostatic voltmeter and switching attachment were used to determine the potential of the accumulated particle mass during a trial of the sensor. It was determined that the effective time required to sample the charged particles at the outlet of an electrostatic precipitator's fields amounted to 20-25 minutes and was determined by their concentration in gases. The total error of determining the aerosol charge when using the device and procedure developed did not exceed 20%. Figure 1; reference 1 (Russian).

UDC [66.092.573:661.7::547.546]:66.097.38

Analysis of Effectiveness of Catalyst Regeneration Regimes in Production of Aniline by Nitrobenzene Hydrogenation*907M0220C Moscow KHIMICHESKAYA
PROMYSHLENNOST in Russian No 3, March 1990
pp 142-143*

[Article by P. B. Babkova]

[Abstract] Operation of 2 industrial productions of aniline involved the use of one and the same industrial catalysts with practically the same nitrobenzene loading and other production conditions the same. The 1st enterprise used a hard regeneration regime and the 2d used a soft regime. In the 1st case, regeneration consumed about 6 hours; in the 2d case it consumed only 3 hours. The number of regeneration operations in the soft regime for a year of service of a catalyst was less than the number for a hard regime. The 1st enterprise performed about 50 operations, on an average, on one contact apparatus while the 2d performed about 101 operations, on the average. Time spent on catalyst regeneration in the 1st contact apparatus was 285 hours for the 1st and 329 hours for the 2d enterprise. Use of a soft regime produced only a slight (44 hours) difference in time spent on catalyst regeneration in one contact apparatus for one year but this difference becomes significant in terms of the entire productive capacity. In case of the 1st enterprise, the increase of productivity of the contact apparatus due to an increase of length of effective recovery was actually achieved at a higher output of aniline from each kilogram of catalyst per year (2475 kg for the 1st enterprise and 2380 kg for the 2d). The increase of the length of interregeneration period in case of the soft regime of catalyst regeneration was attributed to the decrease of rate of recrystallization of the metal phase and the high degree of recovery. Choice of the preferred method of regeneration from the point of view of economy must also consider such factors as the additional use of vapor and gas in case of the soft regime. Figure 1; references 5: 3 Russian; 2 Western.

UDC 66.094.373:678.0.273

Dynamics of Process of Formation of Industrial Catalyst Mass*907M0220I Moscow KHIMICHESKAYA
PROMYSHLENNOST in Russian No 3, March 1990
pp 165-166*

[Article by A. P. Fedoseyev, V. V. Demin, I. N. Mironov and A. V. Bespalov]

[Abstract] Study of the process of extrusion forming of a paste-form type catalyst mass CBC (catalyst of sulfur dioxide oxidation) involved use of a PFSH-30 molder and an industrial catalyst mass, shaped in the form of

cylindrical granules with diameter from 2-8 mm. Determination of productivity of the molder G_i every 2 minutes in the process of extrusion molding and of productivity for the entire period of the experiment G_{av} preceded calculation of the degree of pulsation of productivity (%) as the relationship $G_i - G_{av} / G_{av}$. The extrusion process had a pulsating disordered nature. The degree of pulsation reached its highest value (50-60%) during small values of cross section of the filler (determined by the number of holes) S_c and the diameter of the holes. Increase of S_c from 18 to 25 percent decreased the degree of pulsation to 10 percent. The pulsation period T at small values of S_c (6-10%) was 6-8 minutes but decreased to 3-4 minutes with increase of S_c to more than 20 percent. The pulsations may cause microstresses, external and internal defects of shape of grain of the catalysts and calls for maximally possible smoothing of pulsations. The optimal value of S_c of the former during forming of the paste-form catalyst mass CBC in the form of cylindrical granules of different diameter should be 18-25 percent. Figure 1; references 3 (Russian).

UDC 66.097.3:542.8:547.592.12

Activity of Aluminoplatinum Catalysts in Dehydrogenation of Cyclohexane as Function of Their Preparation Method*917M0007E Leningrad ZHURNAL PRIKLADNOY
KHIMII in Russian Vol 63 No 6, Jun 90 (manuscript
received 24 Jul 89) pp 1318-1322*

[Article by T. M. Klimenko, D. K. Krachilov, A. V. Grishchenko, L. A. Sayko, and V. V. Chulkova]

[Abstract] The activity of aluminoplatinum catalysts in the dehydrogenation of cyclohexane depends on the dimensions of the platinum crystallites formed during the preparation process. The smaller the crystallites' dimensions, the higher their activity. The study reported herein examined the effect that the preparation method and selected promoters have on the activity of aluminoplatinum catalysts in the dehydrogenation of cyclohexane. Three series of catalysts were prepared. In the first series of catalysts the platinum content was kept between 0.05 and 2% by mass, and the catalysts were prepared by impregnating granules of γ -aluminum oxide by three different methods (in the absence of competing acids, with the addition of hydrogen chloride, and in the presence of acetic acid as a competing acid). In the second series, the catalysts contained from 0.25 to 0.36% platinum by mass and various contents of rhenium (from 0.1 to 0.7% by mass) plus acetic acid added as a competing acid. In the third series, the amount of platinum was kept constant at 0.36% by mass with various quantities of tin (from 0.1 to 0.7% by mass) with acetic acid added as in the other series. It was concluded that an even distribution of the applied chloroplatinic acid along the inner surface of the carrier granules increases the catalysts' activity during the dehydrogenation of cyclohexane by permitting full use of the "stabilization centers." It was further found that competing acids block the

weakest adsorption centers of the carrier surface, which results in a reduction of the amount of double and triple platinum clusters on the catalysts' surface. Rhenium was found to stabilize the atomized state of platinum. Finally, tin was found to block the stabilization centers of the platinum's atomized state on the catalysts' surface. Figures 4; references 14: 9 Russian, 5 Western.

UDC 665.658:547.38:66.0973

Features of Hydrogenation of 2-Ethylhexene-2-al-1 on Catalysts Containing Platinum and Palladium

917M0007F Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 63 No 6, Jun 90 (manuscript received 27 Jul 89) pp 1323-1326

[Article by M. G. Katsnelson, N. Ya. Gordina, G. P. Prokopenko, and P. V. Bezzvorotnyy]

[Abstract] Research on the process of the hydrogenation of 2-ethylhexene-2-al on aluminum-zinc-chromium and copper-zinc-chromium catalysts reveals that the hydrocarbon formation reaction occurs as a function of the depth of hydrogenation of the double bond in 2-ethylhexenal. The study reported herein was conducted to select the optimum catalyst in the sense of selective hydrogenation of the double bond, i.e., hydrogenation of 2-ethylhexenal into 2-ethylhexanal, and to determine the effect that the nature of the metal (platinum and palladium) and the nature of the carrier (aluminum oxide and silicon oxide) have on selectivity. Five catalysts (AP-56, AP-64, No 322, No 394-P, and No 391) were studied under a pressure of 1 to 30 MPa in a flow-through circular unit (volume of the catalyst layer, 260 cm³) as well as under atmospheric pressure in a glass tube reactor (volume of the catalyst layer, 80 cm³) with hydrogen fed to flow from top to bottom. The catalysts were reduced to a temperature of 400°C with hydrogen fed in an amount up to 500 parts (by volume) per part (by volume) catalyst. The raw material comprised a fraction of 2-ethylhexenal containing 94-98% of the basic matter and a dimer fraction of the product of the hydroformylation of propylene boiling off between 120 and 180° and containing the following (percent by mass): 2-ethylhexen-2-al-1, 65; 2-ethylhexan-2-al-1, 8-9; butylbutyrates, up to 10; butanols, up to 50.5; and trimers, up to 10. The product was analyzed by the gas-liquid chromatography method on an LKhM-80 MD chromatograph with a 3-m-long column filled with dynochrome plus 10% PEG-20,000. The tests showed that the catalyst containing palladium applied onto aluminosilicate (No 322) had the highest selectivity. It was found that the

specimens containing palladium have a higher hydrogenation capability with respect to the double bond and a higher cracking ability than do specimens containing platinum. Higher cracking and hydrogenation activities appear when aluminum oxide is used as a carrier than when silicon oxide is used. Tables 2; references 2 (Russian).

UDC 665.644.4

Selecting Optimal Catalyst Distribution and Temperature Differentials in Adiabatic Reforming Reactors Based on Isothermal Experiment Results

917M0007G Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 63 No 6, Jun 90 (manuscript received 24 Jul 89) pp 1326-1331

[Article by R. N. Shapiro and Yu. L. Krayev]

[Abstract] The data obtained in studies of the catalytic reforming process on pilot-scale units are generally limited to data on material balance and product quality. When designing and operating industrial units, however, it is essential to have data on thermal effects and the distribution of catalyst throughout the reactors. The study reported herein demonstrated that research conducted on a pilot-scale unit can indeed be used to determine the temperature differentials in reactors and to select the optimum distribution of catalyst throughout the stages of the process. The catalytic reforming of a benzene fraction from 68 to 85° was studied. The studies were conducted on a pilot-scale unit with a specimen of KR-100 commercial catalyst containing 0.36% (by mass) platinum. Squalene was used as the stationary phase, and helium was used as the gas carrier. The make-up of the gaseous products were determined chromatographically. The research conducted yielded a graphic description of the process occurring throughout all the stages in the form of the benzene yield as a function of the arbitrary contact time. The authors also demonstrated a method for calculating the mean isothermal temperature of the catalytic reforming process based on the known temperature at the inlet to the reactors, the temperature differential, and the distribution of catalyst throughout the reactors, and they determined the thermal effect of reforming by using the equation $98 + 310H$ kJ/kg (H being the yield of hydrogen (mass%). Furthermore, they developed a method of finding the optimum distribution of catalyst by adopting the minimum inlet temperature as their optimization criterion. The authors found that for the example considered in their study, using a four stage reactor with a distribution of catalyst in a 1:1.5:2.5:5 ratio made it possible to reduce the temperature at the inlet to the reactor to 485°C. Figures 3, tables 3; references 6 (Russian).

UDC 666.862.011+658.567

Technology of Processing Fluorine-containing Silica Gel Waste*907M0220F Moscow KHMICHESKAYA
PROMYSHLENNOST in Russian No 3, March 1990
pp 153-155*

[Article by G. G. Martirosyan, Yu. S. Sarkizova and E. Kh. Anakchyan]

[Abstract] Results of study of development of a technological process for producing a filler based on silica gel waste which process makes it possible to use completely the AlF_3 and H_2SiF_6 were presented and discussed. An increase of the level of admixtures in the initial silica gel increased the amount of calcium fluoride and especially hydrogarnet which has a good effect on qualitative indicators of the product. Preliminary removal of milk of lime from the coarse particles and admixtures by use of a vibrosieve and hydrocyclones ensured production of a high-quality product. The side product produced, slaked lime, may be used in thickened form by builders or other consumers. The filtrate, produced during filtration of the processed silica gel, is commercial grade water and may be returned to the cycle to produce milk of lime and silica gel suspensions or used to recover dust from waste gases in the scrubber. A flow chart of silica gel waste processing was presented, described and discussed. Figures 2; references 3 (Russian).

UDC 661.257:628.512

Filtration of Gases of Contact Sulphuric Acid Production for Purpose of Removing Nitrogen Oxide (III) From Them*907M0220J Moscow KHMICHESKAYA
PROMYSHLENNOST in Russian No 3, March 1990
pp 167-168*

[Article by M. V. Lobova, V. S. Yepifanov and N. A. Maskayeva]

[Abstract] Study of the possibility of removing nitrogen oxide (III) compounds from process gases of sulfuric acid production before absorption of the nitrogen oxide was discussed. The dependence of the degree of removal of nitrogen oxide (III) compounds on the rate of filtration was determined by experiments. Experiments examined three values of packing of the filter (10, 30 and 80 mm). The degree of purification in the studied range of velocities of the gas, passing through the filter, increased in proportion to the increase of height of the glass fiber layer but the quality of purification decreased with an increase of velocity of the gas. Replacement of the glass fiber felt by glass fiber impregnated with fluorine in some experiments increased gas removal 1.5 times, permitting decrease of the height of the filter 1.5 times for obtaining the same degree of purification. Overshoot of nitrogen oxide (III) compounds from 40 percent for

ordinary glass fiber increased to 80 percent for fluorine-impregnated material as a result of moistening it with 93 percent sulfuric acid at one and the same rate of gas filtration (0.017 m/s). Moistening the material with concentrated sulfuric acid worsened the quality of purification. Data obtained in these preliminary studies may be used to study regularities of the purification process and to create material for filtration of process gases. Figure 1; references 9: 7 Russian; 2 Western.

UDC 661.634.2

Development and Introduction of Technology for Production of Elevated Concentration Wet Process Phosphoric Acid From Common Karatau Ore*907M0292c Moscow KIMICHESKAYA
PROMYSHLENNOST in Russian No 7, July 1990
pp 403-404*

[Article by B. I. Shub, V. F. Karmyshov, N. V. Polyakova, and V. A. Shchegoleva]

[Abstract] An improved process for the production of wet process phosphoric acid of elevated concentration (26-28%) from common Karatau phosphorite ore was developed, which permits one to obtain ammophos fertilizer of higher quality, with an available P_2O_5 level greater than 48%. Laboratory studies indicated that when the process temperature was increased from 75-80 to 88-92, extraction of P_2O_5 was more complete, which improved the crystallization of the phosphogypsum fertilizer obtained and thus improved the yield. The use of a three-filter production scheme reduced P_2O_5 loss during washing. At room temperature the viscosity of the higher concentration phosphoric acid was more than that of the usual product by a factor of 1.5-2.0. However, this difference decreased with increasing temperature and was insignificant over the temperature interval of the technological process. This indicates that the method used to obtain the wet process phosphoric acid does not affect its rheological properties. Scale up of the process gave results similar to those obtained in laboratory experiments, except for a slightly lower washing coefficient, due to the absence of countercurrent washing. The P_2O_5 extraction coefficient was 96-97%. The process proposed makes it possible to obtain higher quality ammophos with decreased expenditures for heat, energy and transportation.

UDC 661.634.2.061.4

Technological Properties of Various Types of Karatau Basin Ore, Used in the Production of Wet Process Phosphoric Acids*907M0292d Moscow KIMICHESKAYA
PROMYSHLENNOST in Russian No 7, July 1990
pp 405-407*

[Article by R. O. Sultankhanova, F. F. Sandt, and P. V. Klassen]

[Abstract] Phosphorite ores found in the Karatau Basin may be divided into six types: high-quality, carbonate,

siliceous, silico-carbonate, pelito-siliceous, and silico-shale. The technological criteria appropriate for use of these raw materials in the production of wet-process phosphoric acid were evaluated. The negative effects of the ratio of MgO , Fe_2O_3 , Al_2O_3 , and the total of K_2O and Na_2O to P_2O_5 , as well as F and insoluble residue on the productivity of phosphogypsum fertilizer filtration and degree of phosphate decomposition were noted when analyzing data obtained over several years. Regression analysis was used to derive a coefficient for each impurity, so that three efficiency coefficients could be calculated for each ore. These coefficients exhibited excellent correlation with experimental results. The degree of weighting of each impurity was different for each type of ore, but iron and aluminum oxides had the greatest effect in all ores. The presence of F blocked the unfavorable effect of MgO . The method presented may also be used to evaluate mixed ores. References 5: Russian.

UDC 661.631.002.3:66.094.22

Electrosublimation of Phosphorus in Processing of Fluxing Pellets

907M0292e Moscow KIMICHESKAYA
PROMYSHLENNOST in Russian No 7, July 1990
pp 407-409

[Article by L. M. Volozhin, G. A. Murzagareyev, and V. V. Avimov]

[Abstract] The recovery of phosphorus from phosphoric fluxing pellets obtained from Dzhanatas layer Karatau Basin ore was investigated. Thermodynamic calculations indicated that at an acidity modulus (M_a) of 1.0-1.2 the equilibrium degree of phosphorus reduction α reached 95.6% at 1500 K. When M_a was less than 1.0, higher temperatures were required for the same extent of reduction. Energy expenditure depended on M_a and temperature. At 1770 K, the greatest yield of phosphorus, 98.5%, was obtained at an M_a of 0.93. A regression equation was constructed which described phosphorus recovery in terms of M_a , temperature and reaction time. Kinetic studies demonstrated that the rate of reaction was greatest at M_a between 0.90 and 0.95, at 1770 K. At M_a above 1.0 the quantity of SiO_2 present exceeded that needed to react with CaO . The excess Si_2 formed polymers which increased melt viscosity and thus retarded the reaction. Increasing M_a also decreased the amount of alkali metal oxides observed in the gas phase. The results indicate that the acidity modulus and composition of the ore must be taken into considerations when establishing the conditions to be used for extraction of phosphorus. Figures 5; references 9: Russian.

UDC 661.632.257:66.046

Ecological Aspects of Phosphorite Pellet Production

907M0292f Moscow KIMICHESKAYA
PROMYSHLENNOST in Russian No 7, July 1990
pp 409-411

[Article by M. P. Talkhayev, S. Ya. Galperina, L. I. Borisova, N. D. Afanasyev, and R. N. Kadyrbekov]

[Abstract] Apparatus for purification of air discharged from phosphorite pellet factories is quite complex and expensive, and is quickly degraded by deposition of inorganic salts, particularly calcium sulfate, on interior surfaces and tubes. Reduction of the level of toxic impurities via process optimization is a more promising approach. It is most important to reduce the residual moisture level in the pellets, by increasing the time they are maintained at 300-600. Decreasing the amount of water vapor which forms during natural gas combustion also lowers the level of fluorine-containing compounds in discharged gases. This may be accomplished by the use of alternate fuel. A different approach involves increasing the recovery of fluorine, phosphorus and sulfur compounds directly from the process of pellet production. The furnace gases are purified in an electrical filter, and then P_2O_5 , and H_2S are absorbed in water. Use of calcined recovered material from wet grinding in the pelletization schist increased the sorption activity of the pellets. The methods described may be combined to significantly decrease the cost of discharge air purification. References 9: Russian.

UDC 66.096.5:66.099.2

Granulation Process in Fluidized Bed During Particle Agglomeration

907M0292g Moscow KIMICHESKAYA
PROMYSHLENNOST in Russian No 7, July 1990
pp 417-419

[Article by V. G. Ostrovskiy, A. S. Parfenov, and Yu. I. Chernyayev]

[Abstract] It has been demonstrated experimentally that during fluidized bed granulation new centers of granule formation are not created and substantial particle agglomeration can not be avoided when working on an industrial scale. This requires continuous addition of new centers for granule formation. Previous methods for calculating the granulometric composition of the system are not suitable for this type of operation; calculation of particle size distribution is difficult. Mathematical expressions for the quantity of particles disappearing from the granulator due to agglomeration in a unit of time and for the mean cubic radius of the commercial-fraction particles found in the granulator at steady state were derived. Practical considerations indicate that the mass fraction and radius of the large particles can vary

only slightly. The results indicate that the granulometric composition in fluidized bed granulation can only be controlled by the rates of material entering and leaving the granulator. When planning apparatus for fluidized bed granulation of low concentration solutions using water vapor heating, it is necessary to have five to tenfold reserves in the transport and milling systems. Figures 1; references 6: Russian.

UDC 665.61.03[574]

Kumkol Oil

917M0009 Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 9, Sep 90 pp 8-9*

[Article by T. O. Omaraliyev, L. Suyunova, I. R. Abdukhaliyeva, Ye. K. Kaldygozov, and S. K. Kerimbekov, Kazakh Chemical Technology Institute]

[Abstract] Oil from the Kumkol field (KASSR) is characterized by the following properties: density at 20°C, 950 kg/m³; ash content, 0.002 (mass%); cokability, 1.67%; viscosity at 50°C, 4.09 mm²/s; solidification point, 10°C; and flash point (in a closed crucible), 19.2°. It contains the following (mass%): silica gel resin, 19.2; carbenes and carboids, 5.8; asphaltenes, 5.4; paraffin, 7.5; and sulfur, 0.064. Its potential content of fractions (mass%) is as follows: up to 180°C, 36.4; up to 350°C, 66.9; up to 500°C, 89.23. Its gasoline fractions are characterized by a low sulfur content and low activity, and it is a good material for catalytic reforming. Its kerosene fractions from 120 to 240°C meet the requirements stipulated in GOST 16564-41 and GOST 10227-62 for the respective fuels TS-1 and RT. Its fractions from 240 to 350°C possess a good quality reserve for producing type L-02-61 diesel fuel (GOST 305-82). The mazout consists of 60% vacuum distillate and 40% bitumen. The Kumkol field is close to the Chimkent Oil Refinery where a mixture of western Siberian oil is processed with gas condensate. This mixture will in turn be processed with the Kumkol oil, which necessitated test distillation of the mixture. Distillation of the mixture in a 9:1 ratio showed that such mixing increases the total output of light fractions to 96.1 mass%, whereas distillation of a 5:5 mixture results in a yield of total light fractions of 59.8 mass%. Kumkol oil thus turns out to be a good raw material for producing motor fuels and can expand the Chimkent Oil Refinery's raw material resources. Tables 2.

UDC 665.666.6

Organonitrogen Compounds of Ashalchinsk Oil From Tatar ASSR

917M0009D Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 9, Sep 90 pp 12-13*

[Article by R. A. Galimov, L. B. Krivonozhkina, G. V. Romanov, and L. M. Petrova, Organic and Physical Chemistry Institute imeni A. Ye. Arbuzov, Kazakhstan Affiliate, USSR Academy of Sciences]

[Abstract] The heavy, high-viscosity oil from the Ashalchinsk field of the Tatar ASSR, which is slated for commercial assimilation, was sampled in order to determine its content of nitrogen-containing compounds. The oils in question were found to contain the following: 6.5-7% asphaltenes, 3.5-4.4% sulfur, 0.4% total and 0.13% basic nitrogen, and 31.6 mg/100 g vanadyl porphyrins. The nitrogen-containing compounds were isolated from the deasphaltate of this oil. This was done by differentiating the nitrogen-containing compounds into compounds that are basic and neutral in nature and to then separate their high- and low-molecular weight components. The four concentrates thus obtained were subjected to mass spectrometric analysis, which revealed that it is neutral nitrogen-containing compounds that predominate among the nitrogen-containing compounds in heavy Ashalchinsk oil. Upon differentiated separation of the nitrogen-containing compounds, the vanadyl porphyrins were distributed primarily in the high-molecular weight nitrous bases. Derivatives of alkylbenzo- and alkylidibenzothiophenes were discovered in the concentrate of low-molecular weight bases. Figure 1, table 1; references 4 (Russian).

UDC 66.074.516.001.8

Commercial Tests of Dust Trap With Internal Circulation of Fluid

917M0010A Moscow *KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 9, Sep 90 pp 6-7*

[Article by V. A. Bagdasarova, A. I. Denisenko, and V. V. Makhanko]

[Abstract] A great deal of dust is released in shotblast barrels when castings are processed. At present, many shotblast barrel aspiration systems are equipped with DP-10A smoke exhaust gas fan-dust traps. The main drawback of this type of cleaning system is the high dust content in the air released into the atmosphere. A two-step gas-scrubbing circuit has been proposed to solve this problem. The first stage consists of a conventional DP-10A combination exhaust fan and dust trap. The second stage of the circuit is a series-produced STsVP 10-80 scrubber device with internal circulation of fluid. Such dust traps effectively trap dust with particles ranging from 2 to 5 μ at a comparatively low pressure loss (1 to 1.3 kPa). The water flow rate ranges from 2 to 5 g per cubic meter of air cleansed of its dust. Commercial tests of the new scrubber yielded good results. The new units had a capacity from 8,200 to 9,200 m³/h and were between 98 and 98.4% effective in trapping dust. The main advantages of the new unit were its low water flow rate, absence of any nozzles or pumps to feed fluid into the device, presence of a small self-contained system to remove slime from the device, and its small overall dimensions and compactness. Three units with STsVP 10-80 scrubbers were installed in the steel-making plant

at Georgiyevsk Fittings Plant, where they were responsible for a significant improvement in ecological and working conditions. Figure 1.

UDC 536.24:621.575.9:661.384

Increasing Heat Transfer Efficiency in LiBr Absorption Refrigerating Machine

917M0010B Moscow *KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian*
No 9, Sep 90 pp 16-18

[Article by A. V. Baranenko, V. M. Zyukanov, candidates of technical sciences, and A. L. Shevchenko]

[Abstract] The technical and economic indicators of LiBr absorption refrigerating machines may be improved significantly by intensifying their heat and mass transfer processes. Using surfactants as intensifiers has aroused interest since the presence of a surfactant on a film of a solution results in a hydrodynamic instability of the interfaces (the Marangoni effect) that is manifested in a change in the balance of the tangential forces on the free surface of the down-flowing film, thus intensifying its heat and mass transfer. Using isooctanol as a surfactant increases the cooling power of an LiBr absorption refrigerating machine by 20-25%. When this is done, however, it is necessary to furnish the refrigerating machine with a special device to circulate the isooctanol with a solution since its low density causes it to accumulate on the surface of the solution in the absorber and in the dead-end portions of the refrigerating machine. In an effort to eliminate the need for a special circulation device, the authors of the study reported herein therefore examined the possibility of using fluorinated surfactants, i.e., four domestically produced (at a cost of 40-50 rubles/kg) fluorinated alcohols, for the intensifier. They conducted experiments on two models of a trickle absorber. The fluorinated alcohol 1H,1H,5H-octafluoropentanol-1 was used as the surfactant. It was discovered that introducing fluorinated alcohol into the LiBr solution significantly intensified heat transfer during the absorption of vapor by the solution film. Adding 1H,1H,5H-octafluoropentanol-1 in a quantity to make a 0.04% solution made it possible to reduce the area of the device's heat transfer surface by 40%. Figures 4; references 15 (Russian).

UDC 621.7.025.7:621.59

Degreasing Cryogenic Equipment by Aqueous Detergent Solutions With New Components

917M0010C Moscow *KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian*
No 9, Sep 90 pp 19-20

[Article by A. M. Domashenko, S. Ye. Narkunskiy, candidates of technical sciences, R. I. Nepomnyashchaya, A. I. Petrova, and L. A. Prusikina]

[Abstract] The branch standard for degreasing equipment recommends various solvents and aqueous detergent solutions. The former have a number of fundamental drawbacks; for example, some solvents damage the ozone layer, and others necessitate the use of complex equipment and strict adherence to the respective safety measures, hence the popularity of aqueous detergent solutions in cleaning cryogenic equipment. In view of the popularity of detergents, the authors of the study reported herein examined the cleaning capability of synthetic detergent preparations recommended by the All-Union Scientific Research Institute of Surfactants. The preparations examined were mixtures of surfactants, alkaline inorganic salts, organic additives (Temp-100, Elva 1, Elva 2M, Labomid-101, Sofal), and oxyethylated monoalkylphenols (Neonol AF9.6 and Neonol AF9.12). During the study, 50x50-mm plates of different materials (aluminum alloys, copper, brass, and steels) were smeared with equal quantities of oil and immersed in a tank containing a detergent solution. The degreasing was performed once or twice in 30-minute cycles, followed by 15-minute intermediate and final rinses. The temperature of the detergent solutions was varied from 40 to 80°C. The temperature conditions were found to have a significant effect on degreasing quality (70-80°C was found to be far better than 40-50°C), as did the detergent concentration in the detergent solution (20 g Neonol AF9.6 per liter removed 10-fold more grease than did a concentration of 5 g/l). On the basis of their experiments, the authors recommended the synthetic detergents Temp-100, Labomid-100, and Sofal as ready-to-use products and Elva 1 and Elva 2M as additives to aqueous solutions of such agents as trisodium phosphate or soluble glass. Neonol AF9.6 and Neonol AF9.12 were recommended as replacements for OP7 and OP10, which are no longer produced. Figures 2, tables 2; references 6 (Russian).

UDC 536.48:621.592.045

Developing Method of Designing Static Magnetic Refrigerator With Diode Coating

917M0010 Moscow *KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian*
No 9, Sep 90 pp 20-22

[Article by V. A. Shaposhnikov, A. P. Grafov, A. V. Kortikov, and L. N. Yefimova, candidates of sciences, and A. V. Likhoboy]

[Abstract] This article deals with developing a method of calculating the efficiency of a static magnetic refrigerator with an allowance for the temperature dependence of the working medium. The static magnetic refrigerator examined, which was intended to transfer heat from the temperature level of He II to a level of 4.2 K, used gadolinium-gallium garnet as its working medium. At temperatures in the range from 1.3 to 4.2 K its heat conduction coefficient changes by more than an order of magnitude; consequently, in an actual cycle there are

cooling power losses caused by processes of nonstationary heat conduction in the working medium. Because of this, the measures to increase the efficiency and cooling power of the static magnetic refrigerator in question entailed a numerical analysis of the effect of the variability of gadolinium-gallium garnet's thermophysical properties, heat transfer conditions on its surfaces, and the actual heat flow from the He I. To eliminate the losses due to the flow of heat to the working medium from the He I, the authors tested several thermal diodes as a thermal switch. In one version they used coated the surface of the working medium that was turned to the He I with monocrystalline silicon. By making a series of calculations they were able to analyze the effect of the

key geometric parameters and temperature gradients in the crystal during the boiling of He I and condensation of He II vapors and discover their relationship to the device's efficiency. The mathematical model and numerical method developed to analyze the processes occurring in static magnetic refrigerators may be used when designing different design versions of such refrigerators, and the thermal diode the authors developed made it possible to significantly increase the efficiency of a static magnetic refrigerator when using He II as its cryogenic agent at low frequencies of change in the magnetic field, which is important in creating such refrigerators with a cooling power of more than 2 W. Figure 1; references 6: 2 Russian, 4 Western.

UDC 536.468.001.24

Calculation of Self Ignition Temperature of Vapors of Polyfunctional Derivatives of Aliphatic Compounds in Air

907M0220E Moscow *KHIMICHESKAYA PROMYSHLENNOST* in Russian No 3, March 1990 pp 148-149

[Article by L. I. Nuzhda and N. M. Polyakov]

[Abstract] Examination of some general features of the dependence of the self-ignition temperature on structure involved acquisition of correlation equations which make it possible to introduce the dependence t_s on the structure of compounds in the form of simple quantitative relationships employed the principle of multilinearity and basic positions of the quantitative theory of organic reactions. From these positions, the structure of the studied compound is compared to the structure of an initial alkane and the latter is considered to be a methane derivative. This made it possible to consider the effect of different structural fragments (atoms, functional groups) in comparison to a standard with the aid of structural constants σ and to assess their values quantitatively. Calculation of the effect of molecular structure of substituted alkanes produced a mathematical model which made it possible to calculate self-ignition temperatures of polyfunctional compounds of the aliphatic series. Some values of t_s calculated by the formula and those determined experimentally were presented. A check showed that the formula obtained adequately matches the experimental data for more than 40 substances considered with a confidence level of 0.95. Standard deviation of results of calculation by the formula from experimental data was 15°C and the maximum error of calculation was 14 percent. References 8: 7 Russian; 1 Western.

UDC 614.833.5:547.461.8

Analysis of Danger of Explosion of Air-dust Mixture of Sebacic Acid in Pneumatic Tube Drier

907M0220L Moscow *KHIMICHESKAYA PROMYSHLENNOST* in Russian No 3, March 1990 pp 178-180

[Article by B. G. Popov and O. V. Serazutina]

[Abstract] In spite of the scarcity of calculated data concerning reliability of pneumatic tube driers, the process of drying and the means of protection, it is possible to obtain tentative values of the risk of an accident and probable material loss from explosion of a hot air-dust mixture in technical devices. The risk of accident was calculated by analysis of a tree of dangerous events. The risk of trauma was determined by the probability of explosion of the air-dust mixture drier and the location of persons in the danger zone. A tree of dangerous events which determine the probability of trauma after an explosion in a pneumatic tube drier and a tree of

dangerous events which determine the probability of the occurrence of sparks of mechanical origin, static electricity sparks, self-ignition of dispersed material and ignition from transfer of flame from equipment around the drier were examined. The possibilities of accidents were calculated and discussed. If these requirements are not met, other safety measures must be provided. Figures 2; references 7 (Russian).

UDC 665.753:665.521.3

Role of Colloid Systems in Formation of Residues by Jet Fuels

917M0009G Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 9, Sep 90 pp 22-24

[Article by Ye. P. Seregin, N. M. Likhterova, V. G. Gorodetskiy, A. F. Gorenkov, I. A. Litvinov, and O. A. Starodubtseva]

[Abstract] The study reported herein examined the phase state of jet fuels with different degrees of purity and aging to discover its effect on the fuels' tendency to form residues during use. Electron microscopy studies were performed on the commercial jet fuels TS-1 and RT and on pilot-production and laboratory specimens, i.e., hydrogenation products. It was discovered that fuels that contained a small amount of disperse phase in the original product were less prone to the formation of residues. The effects of storage on fuel to which 0.003% (mass) ionol had been added and fuel to which no ionol was added were compared. It was found that the heat stability index of the ionol-containing fuel specimens changed periodically, increasing by a factor of 6-7 and then decreasing by a factor of 4-5. The amount of sediment in the filter changed in an analogous manner. The nature of the dependences discovered and the absence of any noticeable consumption of the antioxidant (0.0028%) could not be explained by the theory of liquid-phase oxidation of hydrocarbons. When the fuel studied was looked upon as a heterogeneous system, it was possible to explain the phenomena observed as a consequence of the periodic coagulation of such a system when some critical amount of disperse phase was reached. Although ionol inhibits oxidation processes, it had no effect on the overall nature of the system's transition to a disperse state. Similar changes occurred after 4 months in the samples of fuel that did not contain ionol. It was further found that the rate of change in oxidation stability during storage depends on the ratio of surface contact and volume of hydrofined fuels in the storage equipment. Figure 1, tables 4; references 11 (Russian).

UDC 66.5.61:54.3.[470.4]

Make-Up of Nonhydrocarbon Part of Diesel Fractions of Oils From Ulyanovsk Oblast

917M0009H Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 9, Sep 90 pp 24-25

[Article by I. S. Lazareva, N. M. Kozlova, O. Ye. Shabalina, and L. F. Demkina, Kuybyshev Affiliate, All-Union Scientific Research Institute of Oil Refining]

[Abstract] The diesel fractions of a number of the high-sulfur oils of the new fields in the Ulyanovsk Oblast are characterized by a high acidity (9-17 mg KOH/100 ml). After they are stored for a comparatively short period, they deposit a benzene-insoluble residue on the tank walls. This residue was studied by IR spectroscopy. The residue was dissolved in an alcohol and benzene (35:65) mixture, after which it was applied to a KBr plate in the form of a layer 0.015 to 0.020 mm thick, with the solvent evaporated in air. IR absorption spectra were then taken on a UR-20 spectrophotometer in the 400 to 4,000 cm^{-1}

range. Spectral analysis confirmed the data regarding sulfur, nitrogen, and acid value that were obtained by chemical analysis. Chemical analysis for sulfur content (5.25%) confirmed the presence in the residue of about half the total amount of sulfoxides. The other half comprised amido acids. Similar results were found for the two fractions studied. This study of residues from the diesel fuel fractions of the oils of the Ulyanovsk Oblast represents the first time that amido acids were identified in a mixture with sulfoxides. Figure 1, tables 2; references 2 (Russian).

UDC 621.3.035.2

Manganese and Cobalt Oxide Mixtures as Active Anode Coating in Electrolysis of Diluted Chloride Solutions

917M0007B Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 63 No 6, Jun 90 (manuscript received 30 Mar 89) pp 1254-1257

[Article by V. S. Sorokenkya, R. U. Bondar, T. A. Pistunova, and Yu. G. Olesov, Dnepropetrovsk Chemical Technology Institute imeni F. E. Dzerzhinskiy]

[Abstract] The problem of finding an inexpensive and accessible anode material for the electrolysis of diluted chloride and sulfate-chloride solutions remains critical despite the progress that has been made in creating stable titanium-based anodes. Titanium anodes with an active coating of MnO_2 and Co_3O_4 have recently been recommended for use in such solutions. The study reported herein examined the electrochemical characteristics of titanium anodes with an active coating consisting of a mixture of different compositions of manganese and cobalt oxides. The electrodes were prepared by thermal decomposition of aqueous solutions of a mixture of analytical-grade nitric acid cobalt and manganese salts. Before the solution was applied, the titanium blanks (150x10x1 mm) were cleaned with emery cloth, etched in a mixture of HNO_3 :HF (3:1) acids for 15-30 seconds, and hydrogenated in a 10% solution of oxalic acid at a temperature of 90-95°C for an hour. The generally accepted method was used to apply three layers of coating from a mixture of 30 and 70 mol% RuO_2 and TiO_2 respectively (at 400°C for 10 minutes). Next, 20 layers of active coating of a mixture of MnO_2 and Co_3O_4 were applied. Each layer was dried for 30 minutes at temperatures from 100 to 120°C and roasted in a muffle furnace. An insulating coating was then applied to the nonworking surface of the electrodes, and this resulted in an anode with a working area of 2.5 cm². It was discovered that the selectivity of the MnO_2 -coated titanium anode during electrolysis in diluted chloride electrolytes increased significantly after the addition of cobalt oxide to the active mass (it tripled after the addition of 40-50 mol% Co_3O_4). Titanium-based anodes with a mixed coating (MnO_2 : Co_3O_4) and with a sublayer of RuO_2 and Ti_2 had higher potential values than did the anodes

without a mixed coating. Additional studies examining the corrosion resistance and manufacturing and operating costs of such electrodes are necessary before the feasibility of using them can be adequately determined. Figures 2; references 10 (Russian).

UDC 546.623.33:542.8

Selected Properties of Ceramic Sodium Polyaluminate-Based Electrolyte

917M0007C Leningrad ZHURNAL PRIKLADNOY KHMII in Russian Vol 63 No 6, Jun 90 (manuscript received 26 Jul 89) pp 1257-1261

[Article by M. B. Dergacheva, O. S. Vladimirova, L. A. Lyutsareva, Z. L. Koposova, and N. L. Panova, All-Union Scientific Research Institute of Current Sources and Institute of Organic Catalysis and Electrochemistry imeni D. V. Sokolskiy, KazSSR Academy of Sciences]

[Abstract] Ceramic sodium polyaluminate-based electrolytes are intended for use in Na-S accumulators operating for extended time periods. The study reported herein examined the factors determining the beginning and duration of the electrochemical breakdown of polycrystalline β -alumina, including the threshold current density initiating breakdown in cells with fused sodium at temperatures between 573 and 673 K. The ceramic electrolyte studied was synthesized from domestic commercially produced aluminas (types G-00 and GK) corresponding to the chemical formula $\text{Na}_2\text{O} \cdot 0.175\text{Li}_2\text{O} \cdot 6.1\text{Al}_2\text{O}_3$. Ceramic electrolyte disks 10 mm in diameter and 2 mm thick were prepared for the studies. They were calcined at 1,073 K for 5 hours to remove adsorbed moisture. The electrochemical cell used was a polycore tube (polycrystalline Al_2O_3) based on a ceramic electrolyte disk connected to the tube by glass cement at 1,173 K. The electromotive force method was used as a monitoring method. During the experiments the direction of the current was reversed several times: every hour of electrolysis at densities of 23 and 15 A/cm² and every 2 to 3 hours at 5 and 8 A/cm². It was discovered that the threshold current above which the ceramic electrolyte begins to break down is between 8 and 15 A/cm². Changes in the make-up of the ceramic electrolyte did not affect the threshold current density. Figures 2, tables 4; references 6: 1 Russian, 5 Western.

UDC 628.543

Heat Treatment of Municipal Wastes Sediment With Addition of Natural Zeolite

907M0220D Moscow *KHIMICHESKAYA PROMYSHLENNOST* in Russian No 3, March 1990 pp 145-148

[Article by S. S. Karakhanyan, Z. S. Arakelyan, I. M. Makaryan and Ye. M. Khechumyan]

[Abstract] A study of the possibility of using clinoptilolite of the Noemberyan deposit in ArSSR as a deodorant during drying of sediment from the Yerevan "Aeratsiya" station was described and discussed. The sediment with moisture content of about 77.4 percent, containing a large amount of organic substances rots quickly and produces a foul odor. Determination of the equilibrium pressure of the vapors over the mixture with the zeolite revealed the optimal amount of zeolite required to prevent liberation of gases while drying the sediment. Determination of physico-chemical and thermal characteristics showed the optimal quantity of natural zeolite, which must be added to the sediment to prevent gas liberation while drying, is 23 percent. Application of this amount of zeolite completely eliminated the unpleasant odor and assured decontamination and dehydration of the sediment. The residue can be stored and used as fertilizer. Figures 4; references 8 (Russian).

UDC [661.7:547.332.33].002.68-911.3:66.074.3

Clean up of Gaseous Effluents from Vinylchloride Production

907M0292a Moscow *KHIMICHESKAYA PROMYSHLENNOST* in Russian No 7, July 1990 pp 398-400

[Article by I. D. Bendetskaya, I. G. Isakov, T. Ya. Kolot, and O. V. Gorbus]

[Abstract] Adsorption, catalytic and thermal methods may be used to clean up the gaseous by products of vinylchloride production. However the first two methods have several drawbacks. Sorbents for adsorption methods may not be produced in the USSR, not all toxic components may be removed, and sorbent is lost during purification. Organochlorine compounds have a negative effect on the efficiency of some catalysts, while others are expensive. While the thermal method is the best with respect to simplicity and cost, the presence of dichloroethane, which may degrade to HCl, phosphene or free chlorine, is a complicating factor. Oxygen must often be added to the gaseous effluent. Conditions for conducting thermal clean up were investigated using experimental apparatus with a quartz reactor in an electrical heater oven. Reaction time was varied from 1.5 to 3 sec, temperature from 500-950, and ratio of air to reactants from 0.9 to 3.5. The results obtained indicate that the toxic components are practically completely

converted to carbon dioxide, with no phosgene or chlorine production observed at any temperature. Purification levels around 99.5% were achieved at 900-950. However, hydrogen chloride gas was observed, necessitating a two stage approach for total purification. A schematic for an apparatus using adsorption in the second stage is presented. Figures 2; references 9: 8 Russian, 1 Western.

UDC 628.5431:661.7.002.68

Purification of Waste Water from Toxic Organic Substances

907M0292b Moscow *KHIMICHESKAYA PROMYSHLENNOST* in Russian No 7, July 1990 pp 401-402

[Article by L. P. Signalova and K. A. Galutkina]

[Abstract] The effect of a catalytic system containing equal quantities of cobalt compounds, benzonitrile and benzylamine on the liquid phase oxidation of waste water from various industries was studied. Oxidation was conducted in an autoclave-type apparatus at 200 and 5 Mpa. Practically complete destruction of isovaleric and naphthenic acids was seen at cobalt concentrations of 50-70 mg/L. The best concentration of the nitrogen-containing compounds was found to be 65-85 mg/L. Under optimum conditions, the oxidative process was complete in 8-10 minutes. Waste waters from various industries were mixed to obtain the optimum catalyst concentrations before oxidation. After diluting 1:10 with tap water, the degree of oxidative destruction of organic substances was observed to be 98%. Figures 3; references 6: Russian.

UDC 66.011

Using Electrochemical Method To Synthesize Sodium and Calcium Aluminates To Clean Waste Waters

917M0007A Leningrad *ZHURNAL PRIKLADNOY KHIMII* in Russian Vol 63 No 6, Jun 90 (manuscript received 8 Sep 89) pp 1249-1253

[Article by I. V. Gofenberg, Ye. O. Salnikova, L. Ye. Sitchikhina, and Ye. N. Turanina]

[Abstract] Aluminates of alkaline and alkaline earth metals are among those reagents that may be used to clean soluble impurities such as sulfates from waste waters. These compounds are formed during the reaction of aluminum and its oxide or hydroxide with hydroxides of alkaline (alkaline earth metals). Aluminates may also be produced during the reaction of aluminum oxide or hydroxide with carbonates of alkaline metals at elevated temperatures (by sintering). The main problem in using the first method is the long duration of the process owing to passivation of the initial substances by the reaction products. The main problem with the second method is that it is generally difficult to achieve an end product

with a constant make-up. The electrochemical method is not fraught with either of these problems. Aluminates can be synthesized electrochemically in a non-flow-through electrolyte cell with soluble aluminum electrodes. Different concentrations of NaOH and $\text{Ca}(\text{OH})_2$ solutions were used as the electrolyte. The following reactions occur at the anode and cathode, respectively: $\text{Al} - 3\text{e} \rightarrow \text{Al}^{3+}$ and $2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2 + 2\text{OH}^-$. The consumption of electrical power to produce the reagents was reduced by adding a saturated KCl solution (at a rate of 0.2 g/l) to the electrolyte solution. Since the electrochemical method of producing aluminates entails two

reactions (a chemical one and an electrochemical one), the electrolyte concentration, current density, and duration of the process are key parameters to the process. The authors of the study reported herein established the following as optimal values of these parameters: concentration of the electrolyte solution, 3-4%; current density, 110 to 130 A/m^2 ; and duration of the process, 7.5 to 15 minutes. Besides being simple to implement, the process developed is low in cost, with sodium aluminate costing 0.273 rubles/kg and calcium aluminate costing 0.107 rubles/kg to produce. Figures 3, tables 3; references 6: 4 Russian, 2 Western.

UDC 631.8.095.337.45

Production of Phosphoric Fertilizers With Use of Natural Thermal Waters of Dara-Dag907M0220G Moscow *KHIMICHESKAYA*
PROMYSHLENNOST in Russian No 3, Mar 1990
pp 155-156

[Article by M. S. Alosmanov, Z. M. Bafadarova, Z. R. Ramazanov and A. P. Dzhafarov]

[Abstract] Studies aimed at development of a process of production of phosphoric fertilizers with use of waste sulfuric acid solutions and natural Dara-Dag thermal waters in order to reduce consumption of expensive boric acid required establishment of the effect of basic factors (concentrations of solutions of the mixture of waste sulfuric acids, their percent relationship, temperature norm and initial temperature of the process and quantity of boric acid added) on the quality of the superphosphate. Borosuperphosphate samples obtained met GOST requirements in boron content and in other indicators. Introduction of boron into the reaction mass promoted passage of the superphosphate formation reaction. Regardless of the norm and concentration of the acid, the degree of decomposition of apatite, under the same conditions, was 2.0-2.5 percent higher than that in experiments performed without boron compounds. This resulted, on one hand, from the favorable effect of boron, which regulates crystallization of the solid phase and, on the other hand, by the increase of activity of hydrogen ions in the system because of the boric acid. References 3 (Russian).

UDC 661.632.23.012.7

Assessment of Quality of Phosphorite Meal and Ways of Improving Its Properties907M0220H Moscow *KHIMICHESKAYA*
PROMYSHLENNOST in Russian No 3, March 1990
pp 156-160

[Article by F. V. Yanishevskiy, A. I. Angelov, V. G. Dubinin et al.]

[Abstract] Vegetation experiments were carried out to determine the agrochemical effectiveness of 17 samples of phosphorite meal, representing all operational and promising phosphorite deposits, Syrian and Morocco

phosphorite deposits and deposits from the ocean bottom. Experiments were performed separately with different classes of coarseness of the phosphorite meal (+0.16, -0.16+0.1, -0.1+0.063, -0.063 mm) by applying them under different farm crops on acid sod-podzolic soils of light, medium or heavy mechanical composition, the pH of the salt extract of the KCl of which equals 4.1-4.3. All phosphorite meal samples underwent mineralogical, chemical and physico-chemical analysis and characteristics found from this analysis were presented in a table, described and discussed. Results of the studies stimulated construction, at the Bryansk phosphorite plant, of a new shop which, for the first time in the Soviet Union, will produce finely ground phosphorite meal with content of 29 percent of P_2O_5 from Syrian phosphorite concentrates. Calculation of economic effectiveness of production and use of 1 ton of phosphorite meal of different grinding was presented in a table. Figures 3; references 13: 11 Russian; 2 Western.

UDC 628.33:661.63

Clearing Secondary Steam Condensate in Production of Complex Mineral Fertilizers907M0220K Moscow *KHIMICHESKAYA*
PROMYSHLENNOST in Russian No 3, March 1990
pp 168-170

[Article by V. V. Shatalov, I. V. Nikitin, M. V. Panasyuk et al.]

[Abstract] Development of a continuous antiflow technology for clearing secondary steam condensate employed a pilot device with a thick, moving ionite layer operating in a continuous antiflow regime. The device was illustrated, described and discussed. Basic indicators of operation of the device were presented. The content in the purified condensate of nitrate-ions, fluoride ions, phosphate ions and ammonium ions was 1.86-14.00, 0.10-0.75, 0.07-8.70 and 2.0-3.0 mg/dm³ respectively. Nitric acid and carbon-ammonium regenerates and ionite chains were combined and used to produce ammonium nitrate. The ammonium nitrate content in unified regenerates was 80-120 g/dm³. Monthly productivity of the device in 1988 was 25,000 m³ of condensate at a quality which would not contaminate fishery reservoirs. Development of use of this technology has provided savings of at least 100,000 rubles because of prevention of environmental pollution. Figures 4; references 5; 4 Russian; 1 Western.

UDC 532.73:546.28:548.55

Laws Governing Process of Deep Local Etching of Ceramic Structures in $\text{HF:HNO}_3\text{:CH}_3\text{COOH}$ Compounds

917M0007D Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 63 No 6, Jun 90 (manuscript received 26 Jun 89) pp 1269-1274

[Article by S. O. Izidinov and V. I. Gaponenko]

[Abstract] Deep mesa etching of ceramic structures is an important operation in the technology for producing a number of power semiconductor instruments. Because mesa etching has not been studied adequately with respect to production conditions, the study reported herein examined the process of mesa etching under conditions that were as close as possible to those in actual series production situations in order to discover why the parameters of the mesa relief produced during such processes are not adequately reproducible. The authors studied p-n-p structures 46 mm in diameter in which the p layer was 145-150 μm thick. The structures, which were based on n-type silicon with $\rho = 70$ to 75 Ωcm , were produced by diffusion technology. Five series of tests were conducted on the working side of the structures by thermal oxide-based photolithography. In each series of tests bands 10 mm long and 700, 500, 400, 300, 250, 200, 150, 100, and 40 μm wide were uncovered for etching. The distance between the bands was monotonically reduced from 700 to 300 μm , so about 3 cm^2 on each structure was etched in all of the series. The four structures tested were then subjected to an etching process that simulated actual series production conditions. When the silicons, all of which were $\text{HF:HNO}_3\text{:CH}_3\text{COOH}$ (in a 1 to 5-17 to 1-3 ratio) compounds, were etched, an autocessation process occurred owing to the accumulation of NO_2 in the etching tank that reduced the solution's oxidation power. The conventional approach to creating mesa profiles with a specified depth did not turn out to be sufficiently manageable and correct, particularly under conditions of inadequate mixing intensity. It was concluded that the possibility of an uncontrolled increase in the etching tank's temperature to values exceeding room temperature must be eliminated while still maintaining sufficiently even circulation of the flow of etching agent

around the structures and the optimum volume of etching agent in order to reduce the spread of mesa region parameters and increase their reproducibility within acceptable limits. Figures 2; references 12: 10 Russian, 2 Western.

UDC 541.127:541.124:541.515

Physicochemical Aspects of Redox Reactions of Free Radicals

917M0013C Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 90 (manuscript received 4 Apr 90) pp 2338-2354

[Article by V. D. Pokhodenko, Physical Chemistry Institute imeni L. V. Pisarzhevskiy, UkSSR Academy of Sciences, Kiev]

[Abstract] In the early seventies it was discovered that many reactions of free radicals with different substrates that were previously considered homolytic may include a stage of electron transfer in one of their elementary acts. Free radicals were also discovered to be capable of acting as single-electron reducers of organic and inorganic substrates. The study reported herein examines various physicochemical aspects of the redox reactions of free radicals. The following topics are covered: the kinetics and mechanism of redox reactions occurring between unlike free radicals and ion radicals; the state of stable cation radical salts in condensed media and the effect of the structure of ion pairs on the spectral characteristics of cation radicals; the effect of the electronic structure of a cation radical skeleton, the nature of the anion bound to it, and the medium on the reactivity of cation radicals; electrochemical reactions of free radicals and ion radicals; homogeneous redox catalysis of chemical and electrochemical processes by free radicals (ion radicals); and redox reactions of electron-excited free radicals. The research reported substantiates the possibility of the occurrence of an electron transfer stage as one of the elementary acts of the reaction of unlike free radicals and ion radicals with one another. The capability of free radicals (ion radicals) to act as homogeneous catalysts of chemical, electrochemical, and photochemical reactions is also established. References 55: 49 Russian, 6 Western.

UDC 539.23:546.28

Potentialities of Process of Steam-Gas Levitation Epitaxy of Silicon*917M0007H Leningrad ZHURNAL PRIKLADNOY KHIMII in Russian Vol 63 No 6, Jun 90 (manuscript received 10 May 89) pp 1401-1403*

[Article by Ye. P. Prokopyev]

[Abstract] Chloride and hydride processes of the growth and alloying of epitaxial silicon layers play a prominent role in modern electron materials science. These processes naturally require further development and modification in view of the strict requirements that have been established for uniformity of the properties of built-up epitaxial layers. A new method for the epitaxial build-up of semiconductor layers, i.e., the process of steam-gas levitation epitaxy, has been used to grow layers of GaAs and InP and has been used for InGaAs and InGaAs/InP monolayer structures with sharp alloying profiles and a high degree of uniformity of the thickness of the epitaxial layers grown. The study reported herein examined the possibility of using the steam-gas levitation epitaxy method to grow epitaxial layers of silicon in hydride and chloride processes. Within the framework of the Neumann-Zschauer theory, the authors present a mathematical description of the process of growing and alloying epitaxial layers of silicon for the case of the steam-gas levitation epitaxy method. They derive analytical expressions for the functions of the growth rate $G(h)$ and alloying level $N(h)$ of epitaxial layers, and they analyze the limiting transitions in the case of various modes of implementing the steam-gas levitation epitaxy process. On the basis of the formulas they derive, the authors conclude that the method in question can indeed produce epitaxial layers with a high degree of uniformity under commercial conditions, although they acknowledge that the steam-gas levitation epitaxy method still needs further experimental verification to determine the optimum process parameters. References 6: 3 Russian, 3 Western.

UDC 662.7:678.7(-)139:66.063.6:678.049

Method for Design and Practical Application of Composites With Disperse Filler*917M0013A Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 90 pp 2354-2375*

[Article by G. V. Sakovich]

[Abstract] Thanks to their exceptional diversity and optimal properties, composites are enjoying increasingly wider use. This is particularly true of composites with disperse fillers in a polymer-rubber matrix. The variety of composites is determined by the nature of the disperse filler (metal powders, minerals, organic and inorganic compounds, etc.), type of binder, and additives used. This article reviews the research conducted by the author

and by others on the principles of designing, processing, and using materials consisting of a viscous liquid matrix and solid filler by way of the example of one complex and diverse type of composite, i.e., blended solid fuel. The requirements for blended solid fuels are listed (including high energy characteristics determined by the specific thrust and high fuel density). Since these characteristics are often mutually contradictory, the author presents an expression to obtain the greatest values of each. Listed next are the main components of a generalized scheme of an automated system for primary optimization of different fuel composites on a computer. The main topics covered in the system's existing data base, which currently contains information on about 1,000 fuel components and composites and 1,600 combustion products, are listed. The development of the component base of blended solid fuels (along with fuel binders, plasticizers, vulcanizing agents, other stable additives, and oxidizers) is examined. The rheological properties and the physicomachanical behavior of highly filled systems are discussed, with special emphasis on the use of mathematical models in understanding each of these aspects of the topic. The stability and preservability of composites' properties and the role of research on the kinetics of possible mechanisms of chemical reactions involving blended solid fuels are discussed. The final section, a discussion of the practical application of individual types of composites in the national economy, covers the following: direct use of solid fuels as energy sources, the creation of new processes, and the creation of new materials. Figures 14, tables 3.

UDC 532.783:541.49:547.1'13:546.72:546.56

First Heteronuclear Liquid Crystalline Metal Complex*917M0013F Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 90 (manuscript received 27 Jun 90) pp 2462-2463*

[Article by Yu. G. Galyametdinov, O. N. Kadkin, and I. V. Ovchinnikov, Physical Technical Institute imeni Ye. K. Zavoyskiy, Kazan Scientific Center, USSR Academy of Sciences]

[Abstract] This concise report describes a new substituted ferrocene. The ligand (L) possesses a stable nematic mesophase in the temperature range from 140 to 184°C. A complex with the make-up CuL_2 was obtained by reacting the ligand with copper acetate. The new complex contains three metal atoms and has the properties of a liquid crystal in the temperature range from 221 to 230°C. IR and EPR data indicate that coordination occurs through the nitrogen and oxygen atoms of the ortho-hydroxy group. The CuO_2N_2 node has a close-to-quadratic trans-structure. The procedures for obtaining 4-[2'-oxy-4'-(4"-decyloxybenzoyloxy)benzylideneimino]phenylferrocene (L)] and bis-4-[2'-oleate-4'-(4"-decyloxybenzoyloxy)benzylideneimino]phenylferrocene] copper are detailed.

UDC 542.91:542.97:547.1'13

Organometallic Compounds in Synthesis and Catalysis

917M0013B Moscow IZVESTIYA AKADEMII NAUK
SSSR: SERIYA KHIMICHESKAYA in Russian No 10,
Oct 90 (manuscript received 6 May 90) pp 2211-2228

[Article by I. P. Beletskaya, Moscow State University
imeni M. V. Lomonosov]

[Abstract] By virtue of its position at the junction of organic and inorganic chemistry, organometallic chemistry frequently concentrates on the "hottest" spots of development in chemistry overall. Development of the chemistry of organic derivatives of transition metals began in the middle of this century with the discovery of ferrocene, although some metal carbonyls were known even at the end of the past century. These compounds attracted attention by virtue of their capability of catalyzing different organic reactions. Soviets have made an important contribution to the development of the chemistry of organometallic compounds, particularly in the study of the mechanism of electrophilic substitution at the saturated carbon atom, the chemistry of carbanions and their ion pairs, and the chemistry of anions. The use of transition metal complexes as homogeneous catalysts has made it possible to create new synthesis methods and implement many reactions that previously seemed impossible. Four types of reactions catalyzed by transition metal complexes are particularly important. This first is cross-combination. Over the past two decades it

has enjoyed extensive development as a convenient method of synthesizing a carbon-carbon bond, with cross-combination reactions involving organotin proving to be especially interesting in view of its wide availability and suitability for use in the presence of the most diverse substituents. The second important reaction is carbonylation (particularly RX carbonylation with the participation of nontransition metal complexes, carbonylation of aromatic halogenides, and carbonylation of olefins), and cross-combination reactions involving the formation of a carbon-element bond and reactions in aqueous media account for the two remaining important types of reactions catalyzed by transition metal complexes. The second important aspect of the study of the organometallic compounds is the role of organolanthanides (also referred to as "rare earth elements"). These elements are currently playing an important role in the clarification of theoretical problems, are enjoying extensive practical application in catalysis, and have recently received increased attention in relation to high-temperature superconductivity. The progress made in recent decades with regard to synthesizing unstable organometallic compounds has made it possible to produce and characterize various organic lanthanide derivatives, specifically metal carbonyl lanthanide derivatives and organic lanthanide derivatives of the 2+ type. Among the other applications of such compounds, it has been determined that Grignard-like reagents of lanthanides or organolithium and organomagnesium compounds in the presence of lanthanide salts is of great interest from the standpoint of organic synthesis. References 106: 58 Russian, 48 Western.

UDC 542.91:541.49:547.1'118

Synthesis of Complex**Trans-[(PhP(CH₂NRCH₂)₂PPh)PtCl₂]***917M0013E Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 10, Oct 90 (manuscript received 16 Apr 90) pp 2452-2453*

[Article by A. A. Karasik, Ye. V. Malova, G. N. Nikonov, and B. A. Arbuzov]

[Abstract] Phosphines are known to easily form cis-complexes with PtCl₂, whereas the synthesis of trans-complexes frequently causes problems. This article describes the single-stage isolation of the complex trans-(PhP(CH₂NCH₂)₂PPh)PtCl₂ by reacting 1,5-di-p-tolyl-3,7-diphenyl-1,5,3,7-diazadiphosphacyclooctane with PtCl₂ in a 1:1 ratio in acetonitrile. The preservation of the ligand's structure and composition of the complex were confirmed by the integral intensities of the signals of the methyl, phenyl + phenylene, and methine groups in PMR and IR spectra and by data from elemental analysis. NSR data indicated the coordination of the metal at the phosphorus atom. The IR spectroscopy data provided evidence confirming the complex's trans structure, and the low molar electroconduction excluded the presence of ion structures. References 7: 3 Russian, 4 Western.

UDC 547.26'118

Reaction of Dialkylalkynylphosphonites With Diethyl Ether of Mesoxalic Acid and Nitrile of Trimethylpyrroacemic Acid*917M0016A Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 60 No 8, Aug 90 (manuscript received 26 Dec 88) pp 1706-1711*

[Article by I. V. Konovalova, Yu. G. Trishin, I. S. Dokuchayeva, L. A. Burnayeva, Yu. Ya. Yefremov, T. Yu. Kazanina, V. N. Chistokletov, and A. N. Pudovik, Kazan State University imeni V. I. Ulyanov-Lenin]

[Abstract] The structure of compounds formed during the interaction of trialkylphosphites with activated aldehydes and ketones is largely determined by the nature of the substituents at the carbonyl carbon atom. It was also recently demonstrated that the directions of the reactions of dialkyl ethers of alkynylphosphonic acids with derivatives of α -ketocarboxylic acids also depend on the structural features of carbonyl compounds. The study reported herein examined the reaction of dialkylalkynylphosphonites with diethyl ether of mesoxalic acid and nitrile of trimethylpyrroacemic acid. It was established that in reactions of methyl and ethyl ethers of 1-propynyl-, 2-phenylethynyl, and 3,3-dimethyl-1-butynylphosphonic acids with diethyl ether of mesoxalic acid, the main reaction products are four 1,1-dialkoxy-3,3,6,6-tetraethoxycarbonyl-4-R²-2,7-dioxo-1-phosphabicyclo[3.2.0]hept-4-enes (compounds 1-4). Two substituted 1-phosphabicyclo[3.2.0]hept-4-enes (compounds 5-6) are

also formed during the reaction of dialkyl ethers of 2-phenylethynyl and 3,3-dimethyl-1-butynylphosphonic acids with nitrile of trimethylpyrroacemic acid in boiling benzene. Three of these six compounds (compounds 3, 5, and 6) are colorless crystalline substances, and the other three (compounds 1, 2, and 4) are very viscous vacuum-distilled yellow fluids. The structure of the six heterocycles was unequivocally determined by way of the example of 3,6-di(tert.-butyl)-4-phenyl-3,6-dicyano-1,1-diethoxy-2,7-dioxo-1-phosphabicyclo[3.2.0]hept-4-ene (compound 6) by x-ray analysis. It was established that a molecule of this compound has a bicyclic frame with a pentacoordinated phosphorus atom. The P-O² and P-O⁷ bonds of the bicyclic fragment are located in axial positions, while the P-O³, P-O⁴, and P-C⁵ bonds are located in equatorial positions. Tables 2; references 6: 5 Russian, 1 Western.

UDC 547.26'118

Tris(2,2,3,3-Tetrafluoropropyl)phosphite in Reaction With Bromine. Intermediate Quasiphosphonium Structures*917M0016B Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 60 No 8, Aug 90 (manuscript received 7 Dec 88) pp 1711-1718*

[Article by Ye. N. Ofitserov, V. F. Mironov, Sinyashina, T. N., Chernov, A. N., Ilyasov, A. V., Konovalova, I. V., and Pudovik, A. N., Kazan State University imeni V. I. Ulyanov-Lenin and Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Department, USSR Academy of Sciences]

[Abstract] The uniqueness of the reaction of 2-(2,2,3,3-tetrafluoropropoxy)-4,5-benzo-1,3,2-dioxaphospholan with bromine lies in the fact that introduction of the tetrafluoropropyl radical into the P(III) atom results in both an increase in the stability of the resultant phosphorane as compared with its ethyl analogue and in the realization of other ways of stabilizing dibromophosphorane besides Arbuzov's reaction. The intermediate 2-(2,2,3,3-tetrafluoropropoxy)-4,5-benzo-1,3,2-dioxaphospholan disproportionates to phosphoranes with one or two benzodioxaphospholan cycles and bromoanhydrides and forms phosphate. These features make the phosphite described similar to 2-phenoxy-4,5-benzo-1,3,2-dioxaphospholan, which contains a phenyl group that is incapable of dealkylation. Because the authors of the study reported herein hypothesized that the same laws should be observed for the reaction of acyclic phosphites with bromine upon substitution of the alkyl radicals by fluoroalkyl groups, they studied the mechanism of the reaction of phosphite with bromine under various conditions by using the method of low-temperature ³¹P-[¹H] NMR spectroscopy. They discovered that depending on the ratio of reagents and the order in which they were mixed, the solvent, and the temperature, the reaction results were very different.

After conducting several series of reactions, they concluded that in a reaction with bromine, tris(2,2,3,3-tetrafluoropropyl)phosphite is closer in behavior to triphenylphosphite than to conventional trialkylphosphites and forms two types of quasiphosphonium particles, i.e., tris(2,2,3,3-tetrafluoropropoxy)bromo- and tetrakis(2,2,3,3-tetrafluoropropoxy)phosphonium of bromide, which are unstable and break down into bromophosphate and phosphate. The paths of the transformation of the intermediate mono- and dibromophosphates are modeled. Figure 1, tables 2; references 18: 10 Russian, 8 Western.

UDC 547.26'118

Reactions of Organic Hydridophosphines With Azomethines and N-Phenylbenzimidoyl Chloride

917M0016C Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 60 No 8, Aug 90 (manuscript
received 6 Feb 89) pp 1718-1722

[Article by G. V. Romanov, T. Ya. Ryzhikova, and A. N. Pudovik, Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Department, USSR Academy of Sciences]

[Abstract] In an effort to further research the reactions of organic hydridophosphines with compounds having multiple bonds, the authors of the study reported herein examined the reaction of trimethylsilylphenylphosphine with azomethines and N-phenylbenzimidoyl chloride. They discovered that the main products of the reaction of trimethylsilylphenylphosphine with benzalaniline is silylphosphine and that the main product of the reaction of trimethylsilylphenylphosphine is secondary phosphine. They hypothesized that the reaction proceeds through the initial formation of a bipolar ion A that may be stabilized in one of two directions. Silylphosphine is formed when the proton migrates to the negatively charged nitrogen atom, while secondary phosphine is formed in the case of migration of the trimethylsilyl group. Introducing a bulk substituent to the nitrogen atom shifted the equilibrium toward the formation of a product with a P-Si bond. The authors also reacted trimethylsilylphenylphosphine and phenylphosphine with N-phenylbenzimidoylchloride. The first of these two reactions resulted in the formation of bis(N-phenylbenzimidoyl)phenylphosphine, and the second resulted in the formation of bis(N-phenylbenzimidoyl)phenylphosphine. References 10: 5 Russian, 5 Western.

UDC 547.241

Halogenotropy in Dyad P-C. III. Transformations of α -Bromoalkylphosphonites

917M0016D Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 60 No 8, Aug 90 (manuscript
received 9 Sep 88) pp 1722-1727

[Article by O. I. Kolodyazhnyy, D. B. Golokhov, and S. N. Ustenko, Bioorganic Chemistry Institute, UkSSR Academy of Sciences, Kiev]

[Abstract] The authors of the study reported herein previously discovered that P-chlorides containing atoms of hydrogen, chlorine, alkyl, or alkoxy groups at the carbon atom regroup into α -chloroalkylphosphonites and that the regrouping is accompanied by 1,2-(P \rightarrow C)-migration of the chlorine atom and the transition of the phosphorus atom from a pentavalent to a trivalent state. In an effort to continue this line of research, the authors reacted bis(diisopropylamido)alkylphosphonites with bromotrichloromethane in order to examine the migration of other halogen atoms, particularly the bromine atom, in the P-C dyad. After conducting a series of reactions, they concluded that P-bromylides containing atoms of hydrogen, chlorine, bromine, or a methyl group at the α -carbon regroup into α -bromoalkylphosphonites as a result of a 1,2-(P \rightarrow C)-bromotropic shift. They further concluded that bis(diisopropylamido)- α -bromoalkylphosphonites manifest properties characteristic of both compounds of trivalent phosphorus and P-bromylides. This was explained by the existence of phosphorus-carbon dyad bromotropy. Figure 1; references 5 (Russian).

UDC 547.26.118+547.241

Synthesis of S-Alkylalkylchlorothiophosphonates and Their Reactions With Phenols, Mercaptans, and Amines

917M0016E Leningrad ZHURNAL OBSHCHEY
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received 22 Mar 1989) pp 1735-1739

[Article by N. N. Zalesova, L. S. Butorina, E. Ye. Nifantsev, and T. A. Mastryukova, Institute of Elementoorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow]

[Abstract] S-Alkylalkylchlorothiophosphonates are among those compounds that have been relatively little studied. They may be produced by reacting methylchlorophosphine with sulfenclorides in sulfur dioxide. Another way of producing them is from O,S-dialkylmethylphosphonate under the effect of phosgene. The most convenient way of producing them is by reacting mercaptans with the dichloroanhydride of methylphosphonic acid in ether in the presence of triethylamine, but the product yield amounts to only about 30%. The main drawback of all these methods is that they necessitate working with toxic reagents (mercaptans, phosgene, or liquid sulfur dioxide). For this reason, the authors of the study reported herein set out to develop a more suitable method of synthesizing S-alkylalkylchlorothiophosphonates in order to be able to produce various derivatives on their basis. They used chloroanhydrides of methyl- and cyclohexylthiophosphonic acids as the initial product. In the first stage of their experiments, the authors produced disodium salts of methyl- and cyclohexylthiophosphonic acids (yields, 84 and 67%, respectively) by alkaline hydrolysis with

heating in a water-dioxane medium. Next, they produced di- and trisodium salts of selected thioacids of phosphorus. The disodium salts of alkylthiophosphonic acids were treated with halogenalkyls; then, after replacing the solvent by CCl_4 , they were treated with phosphorus pentachloride. It was thus possible to produce S-alkylalkylchlorothiophosphonates with a 54-65% yield. In a separate experiment the authors demonstrated that alkylation of disodium salts results in sodium S-alkylalkylchlorothiophosphonates. The later were easily reacted with phenols in the presence of triethylamine in a benzene solution at 0-4°C. The authors were thus able to produce O-aryl ethers, amides of thiophosphonic acids, and dithioethers of dithiophosphonic acids by reacting S-alkylalkylchlorothiophosphonates with the appropriate nucleophilic reagents. Table 1; references 8: 6 Russian, 2 Western.

UDC 547.753.241

Methylenephosphorylated Derivatives of 1,3,3-Trimethyl-2-Methylene Indoline

917M0016F Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 60 No 8, Aug 90 (manuscript received) pp 1752-1761

[Article by A. A. Tolmachev, A. N. Kostyuk, E. S. Kozlov, and A. M. Pinchuk, Organic Chemistry Institute, UkSSR Academy of Sciences, Kiev]

[Abstract] It has recently been established that in the presence of triethylamine, phosphorous and phosphoric acids react easily with 1,3,3-trimethyl-2-methylene indoline, with the resultant formation of completely stable halogenanhydrides. It is not possible to isolate analogous halogenanhydride with residues of other enamines on account of their low stability. The chemical properties of chloroanhydrides have been virtually unstudied. The study reported herein produced and studied the properties of methylenephosphorylated derivatives of indoline with various substituents at the phosphorus atom. The authors' purpose in undertaking the study was to gather data that could be used in developing methods of phosphorylating other enamines and to determine whether, because methylenephosphorylated indolines are vinyl analogues of amides of phosphorus acids, they would manifest any interesting analogies with the former from the standpoint of their chemical properties. The authors gathered data on the yield, melting and boiling points, and NMR spectra of over 20 methylenephosphorylated derivatives of 1,3,3-trimethyl-2-methylene indoline that, unlike other types of phosphorylated enamines, turned out to be stable compounds. Analogies between their chemical properties and those of the amides of phosphorus acids were discovered. Tables 2; references 10: 3 Russian, 7 Western.

UDC 547.341

Dimethylhydrazones of Phosphorylacetaldehydes

917M0016G Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 60 No 8, Aug 90 (manuscript received 29 Nov 88) pp 1761-1766

[Article by B. G. Liorber, V. V. Zverev, Z. M. Khamatova, V. A. Pavlov, M. V. Alparova, and V. M. Vakar, Kazan Institute of Chemical Technology imeni S. M. Kirov and Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Department, USSR Academy of Sciences]

[Abstract] A series of nitrogen-containing phosphorylacetaldehyde derivatives have been described elsewhere. The study reported herein examined the synthesis of dimethylhydrazones of phosphorylacetaldehydes, compared their electronic structures with those of their nonphosphorylated analogues, and examined their salt formation reactions. The dimethylhydrazones of phosphorylacetaldehydes were obtained by reacting phosphorylacetaldehydes with 1,1-dimethylhydrazine. The hydrazones were synthesized at room temperature. IR spectroscopy and proton magnetic resonance data gathered during an examination of the compounds' salt formation reactions revealed that the amine atom of the nitrogen in the hydrazone fragment is the protonation and quaternization center. Analysis of the photoelectron and electron spectra obtained indicated that the energies and make-up of the upper occupied and lower free orbitals of the dimethylhydrazones of phosphorylacetaldehydes are close to those of aliphatic aldehydes. The methylene group was found to block the interaction of the orbitals of the hydrazone and phosphoryl fragments. Figures 2, tables 3; references 10: 8 Russian, 2 Western.

UDC 547.341

Phosphorylation of Halogen- and Phosphorus-Substituted Divinyl Sulfides

917M0016H Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 60 No 8, Aug 90 (manuscript received 12 Dec 88) pp 1780-1789

[Article by V. G. Rozinov, V. Ye. Kolbina, V. I. Don-skikh, G. V. Ratovskiy, G. V. Dolgushin, G. M. Gavrilova, V. I. Gostevskaya, and S. B. Amosova, Irkutsk State University]

[Abstract] The reaction of divinyl sulfide and α,α' -bis(chloromethyl)divinyl sulfide with phosphorus has been found to result in the formation of 1,4-thiaphosphines. The phosphorylation of α - and β -halogen-substituted divinyl sulfides has not been studied previously. The study reported herein examined the reaction of phosphorus pentachloride with di(1-chlorovinyl)sulfide, di(1-bromovinyl)sulfide, and di(2-bromovinyl)sulfide synthesized in accordance with a method described elsewhere. It was established that derivatives of 1,4-thiaphosphines are formed when α,α' -dihalogen-substituted divinyl sulfides and divinyl sulfide

are reacted with phosphorus pentachloride. It was further determined that such formation of 1,4-thiaphosphines is preceded by the formation of acyclic phosphorus-containing divinyl sulfides (although these compounds were not actually isolated, their existence during the course of the reactions conducted was confirmed by NMR data). It was further concluded that phosphorylation of β,β' -dibromodivinyldisulfide culminates in the stage of the formation of acyclic phosphorus-containing dibromodivinyldisulfide. Finally, the authors found that 2-(dichlorophosphoryl)divinyldisulfide is phosphorylated by phosphorus pentachloride with the participation of a free vinyl group. Figure 1, table 1; references 10 (Russian).

UDC 541.49:(546.742+546.562)

Coordination in Heteroligand and Polynuclear Aminotrimethylenephosphonates of Cu(II) and Ni(II)

917M00161 Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 60 No 8, Aug 90 (manuscript
received 2 Dec 88) pp 1789-1795

[Article by R. R. Amirov and Z. A. Saprykova, Kazan State University imeni V. I. Ulyanov-Lenin]

[Abstract] The study reported herein is a continuation of research on the laws governing the formation of polynuclear and heteroligand complexes of Cu(II) and Ni(II) with the participation of phosphonic acids. In their previous reports, the authors established the formation of a series of Cu(II) and Ni(II) compounds with aminotrimethylenephosphonic acid with the general formula $[MH_nT]$ and determined their stability, relaxation, and spectral parameters. The EPR spectra of frozen solutions of complexonates of Cu(II) and Ni(II) were recorded on an RE-1307 instrument at 77 K. It was discovered that deprotonated aminotrimethylenephosphonates of Cu(II) and Ni(II) have a trigonal bipyramidal structure that is maintained during the formation of heteroligand particles with monodentate ligands. In heteroligand complexonates of Ni(II), the coordination of bidentate ligands changes its structure to octahedral. In the case of Cu(II) this was only detected for ethylenediamine. Spectral data on nine Cu(II) and Ni(II) complexes are presented. In addition, by using the method of computer mathematical modeling with the CPESP program and by processing their set of experimental data over a broad concentration range, the authors determined the optimized values of the formation equilibrium constants of both heteroligand complexonates and calculated their stability ($\lg B[CuT(enH)]$ was found to equal 19.83 and $\lg B[NiT(en)]$ was found to equal 20.21). Figures 3, table 1; references 19: 8 Russian, 11 Western.

UDC 547.241

Dichlorophosphonites and Chlorophosphinates Containing Adamantane Fragment

917M0016J Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 60 No 8, Aug 90 (manuscript
received 2 Dec 1988) pp 1795-1799

[Article by B. I. No, Yu. L. Zotov, and V. N. Karev, Volgograd Polytechnic Institute]

[Abstract] Chloroanhydrides of phosphorus acids are valuable starting compounds in organophosphorus synthesis. The synthesis of chloroanhydrides of phosphorus acid having a hydrocarbon fragment of the structural frame in their molecule make it possible to study the effect of electronic and spatial factors on their reactivity and to produce substances with useful practical properties. The literature describes several chloroanhydrides of phosphorus acids; however, producing them is often a multistage process. During the course of their research on the reaction of adamantane and 1,3-dimethyladamantane with phosphorus trichloride, the authors of the study reported herein discovered that in the presence of aluminum chloride the reaction entails the release of hydrogen chloride. Processing the reaction mass with pyridine and subjecting it to vacuum distillation results in a product identified as 3,5-dimethyladamantyl-1-dichlorophosphine. Because 1,3-dimethyladamantane is produced by isomerization of perhydroacenaphthene in the presence of anhydrous aluminum chloride, the authors were able to combine the stages of isomerization of perhydroacenaphthene and phosphorylation of 1,3-dimethyladamantane and to thus produce 3,5-dimethyladamantyl-1-dichlorophosphine with a satisfactory yield in a single-stage synthesis process. The make-up and structure of the five compounds synthesized during the course of the study were examined by element analysis and IR and PMR spectroscopy. The low reactivity of the phosphorus atom in diadamantylchlorophosphinate in electrophilic reactions was linked to steric difficulties. The reaction of the bromination of the adamantyl fragment was found to be highly dependent on the electron acceptor effect of the chlorophosphoryl substituent in the adamantane nucleus. Tables 2; references 6 (Russian).

UDC 548.737+547.26'118

Crystalline and Molecular Structure of P-(N'-Tolylbenzohydrazonoyl)-O, O-Diethyl-N-n-Nitrophenylimidodiphosphonate

917M0016K Leningrad ZHURNAL OBSHCHEY
KHIMII in Russian Vol 60 No 8, Aug 90 (manuscript
received 21 Dec 88) pp 1799-1805

[Article by A. N. Chernega, S. K. Tupchiyenko, and A. D. Sinitsa, Organic Chemistry Institute, UkSSR Academy of Sciences, Kiev]

[Abstract] Previously unknown phosphazo compounds with a hydrazonoyl group at the phosphorus atom were

recently synthesized by reacting benzhydrazonoylchlorides with anilidophosphites. The polar solvents for the compounds produced are characterized by prototropic migrations in the triad C-N-N, with the position of tautomeric equilibrium being strongly affected by the nature of the substituents in the phenyl nuclei. By analogy with arylformazanes, different geometric isomers are possible for phosphazo compounds. IR and NMR spectroscopy investigations of these compounds showed that in solution in carbon tetrachloride they exist in the form of one of two types of chelates with an intramolecular hydrogen bond. To confirm the preference of one of the two types of chelates and to obtain more information on the molecular geometry of this new class of phosphazo compound, the authors of the study reported herein performed x-ray studies on a representative phosphazo compound, i.e., P-(N'-tolylbenzhydrazonoyl)-O,O-diethyl-N-n-nitrophenylimidophosphonate. Two symmetrically independent molecules were found to exist in a crystal of the study compound; the differences between their molecular structures were found to be very different, however.

Detailed data on the lengths of the bonds and valence angles in each of the two independent molecules are presented along with detailed data on the coordinates of the hydrogen and nonhydrogen atoms and their isotropic and equivalent isotropic temperature factors in the structure of P-(N'-tolylbenzhydrazonoyl)-O,O-diethyl-N-n-nitrophenylimidophosphonate. The authors made special mention of the significant shortening of the N¹-C⁵ bond, which they attributed to the conjugation between the nearly parallel π -systems of the P=N¹ double bond and the C⁵-C¹⁰ benzene cycle. The bond lengths and valence angles in the phosphorus-containing group of both independent molecules were found to be usual. The nitro group was found to be practically in the plane of the C⁵-C¹⁰ benzene cycle, and because of the significant thermal fluctuations of the C atoms of the end ethyl groups, the C-C bonds in these groups turned out to be significantly shortened. It also was noted that only Van der Waals reactions are present between the molecules in the crystal; there are no shortened intermolecular contacts. Tables 4; references 10: 6 Russian, 4 Western.

UDC [66.094.403.661.7::547.332.33]:541.127

Kinetics of Vinylchloride Chlorination

907M0220A Moscow *KHIMICHESKAYA
PROMYSHLENNOST* in Russian No 3, Mar 1990
pp 137-140

[Article by A. I. Rozlovskiy]

[Abstract] Results of independent studies of the kinetics of vinylchloride chlorination were compared to one another and to calculated values of reaction rates established on the basis of existing ideas about the mechanism of the reaction. The studies confirmed that ideas concerning equilibrium dissociation of chlorine give approximately correct ideas about kinetic regularities of vinylchloride chlorination. In cases in which chlorination proceeds predominantly according to a heterogeneous mechanism, the difference between the rate constant of k_1 and k_{ex} (experimental) reached 3 orders of magnitude but was insignificant under conditions of degeneration of the heterogeneous process. Comparison of k_1 and k_{ex} for each chlorination process made it possible to judge whether or not equilibrium of chlorination dissociation reactions may be achieved and how perturbation from possible side processes with participation of chlorination products may affect it. Figures 1; references 15: 13 Russian; 2 Western.

UDC 665.63:[661.7:547.652.1]

Naphthalene Extraction From Hard Resin Pyrolysis

907M0220B Moscow *KHIMICHESKAYA
PROMYSHLENNOST* in Russian No 3, Mar 1990
pp 140-142

[Article by G. B. Lekhova, G. D. Kharlampovich, Ye. B. Novikova et al.]

Studies of rectification of naphthalene-containing fractions of hard resin pyrolysis of different quality employed continuous action rectification equipment with efficiency of 30 theoretical stages for a dichloroethane-gasoline mixture. The study showed that extraction of naphthalene from hard resin of pyrolysis of petroleum raw material may be achieved by sequential realization of the following steps of processing: fractionation of hard resin of pyrolysis into distillate and pitch in flash vaporization; extraction of the 190-270°C fraction on a 2-column unit in the form of the main product of the 2d column; hydrogenation purification of unsaturated hydrocarbons and hydroalkylation of indane homologs. The naphthalene produced may be used to produce C-3 superplasticizer for concrete, phthalic anhydride and purified varieties of naphthalene. References 13: 11 Russian; 2 Western.

UDC 665.61.033[470.66]

Oil From Chingiz Field

917M0009B Moscow *KHIMIYA I TEKHOLOGIYA
TOPLIV I MASEL* in Russian No 9, Sep 90 pp 9-10

[Article by B. T. Dzhetpisov, Dzh. Koshebekov, and T. M. Bisenova]

[Abstract] The oil of the Chingiz field is one of a number of oil sources recently discovered in the region around the Caspian Sea. A specimen taken from the field's No 12 well was analyzed in order to develop the optimal process for refining it. The specimen was found to be light (density at 20°C, 823.4 kg/m³), low in viscosity (8.7 mm²/s at 20°C), resinous (0.27% asphaltenes and 5.64% silica gel resins), high in paraffin (7.3%), low in sulfur (0.26%), and characterized by a low solidification point (-15°C). It had a significant content of light fractions (26% by mass up to 200°C and 56% by mass up to 350°C). The oil is also characterized by a high content of gasoline fractions. The fractions up to 200°C meet the requirements stipulated in GOST 1012-72 for aviation fuels. The fractions from 120 to 230°C and from 120 to 240°C are low in sulfur; however, because of their low viscosity and density they do not meet the requirements specified in GOST 10227-62 for jet fuel. The fractions from 180 to 350°C and from 200 to 320°C meet the requirements set in GOST 305-82 for grade 3 diesel fuel, and the fraction from 350 to 460°C meets the main requirements of a raw material for catalytic cracking. The oil residues are characterized by high viscosity and a low sulfur content (less than 1 mass%), and the residue above 400°C meets the requirements in GOST 10585-75 for mazout. Tables 4.

UDC 665.55:547.26:666.62

Organosulfur and Organonitrogen Compounds of Oil of Kotyrtas Field

917M0009C Moscow *KHIMIYA I TEKHOLOGIYA
TOPLIV I MASEL* in Russian No 9, Sep 90 pp 10-11

[Article by N. S. Buyanova and S. M. Yagyareva, Petrochemistry and Natural Salts Institute, KaSSR USSR Academy of Sciences]

[Abstract] With the exception of the oil from its No 5 well, the Kotyrtas field's oils are heavy (density, 840.1 to 899.8 kg/m³). They are methane-type oils, with between 68.82 and 80.85% of their mass consisting of methane hydrocarbons and between 9.72 and 19.65% consisting of aromatic hydrocarbons. Some oils of the Kotyrtas field are low in sulfur (total content, between 0.356 and 0.5% by mass) while others are not (more than 0.5% by mass). They do not, however, contain disulfide and hydrogen sulfide. Most of the sulfur compounds detected were in the form of either sulfide or residual sulfur. The nitrogen distribution in samples taken from four different wells throughout the field varied greatly. In fractions up to 150°C the content of basic nitrogen is insignificant, but it increases as the fractions become

heavier. Thus, the oils of the Kotyrtas field are mainly low in sulfur content and contain a small amount of mercaptans (with the exception of the oil from well No 24, where such mercaptan sulfur compounds amounted to 11.85% by mass). The oils contained up to 0.83% total nitrogen and up to 0.4547% basic nitrogen. Tables 4; references 5 (Russian).

UDC 577.17:547.912:552.578.3[574.1]

Features of Distribution of Microelements in High-Viscosity Oils and Bitumens of Western Kazakhstan

917M0009E Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 9, Sep 90 pp 13-15*

[Article by S. F. Bakirova, S. M. Ospanova, and V. P. Solodukhin, Petrochemistry and Natural Salts Institute, KaSSR Academy of Sciences, and Nuclear Physics Institute, KaSSR Academy of Sciences]

[Abstract] The x-ray spectral and neutron activation methods were used to study the microelement make-up of the oil and bituminous rocks of the Mortuk, Karaganda, Akbulak, Karamurat, and Tyubkaragan deposits and of selected high-viscosity western Kazakhstan oils and their residues. The samples, which were taken by the "averaged" method, were cleansed of mechanical impurities, water, and soluble salts. After the oil or organic fraction of the oil and bituminous rock was incinerated, the content of microelements in the sol was analyzed. The microelement make-up of the source samples of oil and bituminous rock and their mineral components was also analyzed. All of the specimens studied were characterized by a high aluminum concentration (up to 73,000, 41,000, and 2,600 g/t for the source oil and bituminous rock and its mineral and organic parts, respectively). The nickel content of the specimens varied from borehole to borehole and ranged from 35 to 11 g/t. The vanadium content varied from 4.6 to 430 g/t, and the titanium content ranged from 500 to 4,900 g/t. The cobalt, chromium, copper, and lead contents ranged from 0.25 to 90 g/t, and the scandium content varied by more than an order of magnitude from one well to the others. Dysprosium, uranium, and samarium were evenly distributed in the study specimens. Because of the wide variation in the microelement contents of specimens taken from nearby areas, it was concluded that the natural bitumen of each individual field must be subjected to a separate detailed study. When the microelement contents in the oil and bituminous rock specimens studied were compared with their average values for sedimentary rock, it was concluded that the following elements could be of commercial interest in the Akbulak and Mortuk fields: vanadium (430 g/t), uranium (12 g/t), and molybdenum (74 g/t). Tables 3; references 4 (Russian).

UDC 547.741:553.982:538.113

Distribution of Vanadium in Oils of Western Kazakhstan

917M0009F Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL in Russian No 9, Sep 90 pp 15-16*

[Article by R. N. Nasirov, K. Baymagambetov, M. U. Mukhanova, and T. T. Omarov, Petrochemistry and Natural Salts Institute, KaSSR Academy of Sciences]

[Abstract] Samples of oils from three areas of western Kazakhstan (the Caspian basin, the Buzachi Peninsula, and the Embinskiy region) were subjected to electron spin resonance (ESR) studies to determine the distribution of vanadium in them. The highest vanadium concentration was found in the oils of the Buzachi Peninsula. Several types of porphyrins were also detected in the oils of the Volga and Ural interfluvies. Vanadium was found to be virtually absent in fractions <400°C of the oil of the Gryadovaya field. In the residues, vanadium was found to be primarily in the form of vanadyl porphyrins. Besides a line indicating tetravalent vanadium, the spectra of many Kazakhstan oils also contained an absorption line belonging to a free radical connected with the condensed aromatic structure of asphaltenes. The ESR method was also used to examine the vanadyl porphyrin distribution by components of the oil from the Kara-Arna field. An ESR signal indicating a vanadyl porphyrin complex was found, but the ESR signal indicating free radicals was absent. An ESR signal indicating free radicals was also absent in the spectra of the heavy oils. The spectra of light oils extracted by n-pentane did not contain either an ESR signal indicating vanadyl porphyrin complexes or a signal indicating free radicals. The conclusion that vanadium in the form of vanadyl porphyrins is concentrated in the pitch-and-asphaltene portion of the oil was confirmed, and the absence of an ESR signal indicating free radicals confirmed the absence of asphaltenes. Figures 2, tables 3; references 4: 3 Russian, 1 Western.

UDC 669.295:620.193.462

Method for Protecting Titanium and Its Alloys in Sulfuric Acid Medium Against Corrosion by Titanyl-Ion Inhibition

917M0010F Moscow *KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE in Russian No 9, Sep 90 pp 23-24*

[Article by S. A. Glazkova, candidate of technical sciences, T. N. Karasyuk, and S. G. Bocharova]

[Abstract] It has previously been established that hydrogen absorption by titanium VT1-0 and the alloys AT3 in sulfuric acids is only observed when they are either completely or partially passivated, and this results in the formation of a TiH₂ hydride layer that absorbs hydrogen intensely. An oxide film preventing hydrogen penetration forms on the surface of titanium and its alloys in a stable passive state. Titanium may be brought

to a stable passive state by introducing alloying agents into it or by adding an inhibitor to the acid. Analysis of the literature showed that titanyl-ion (TiO^{2+}) meets the requirements set for an oxidizing agent. Although the effect of TiO^{2+} in concentrated sulfuric acid has been examined previously, its inhibiting effect has not been established. The study reported herein was conducted precisely to establish the corrosion-inhibiting effect of TiO^{2+} . The experiments were conducted in a 1.5% sulfuric acid solution at 95°C in accordance with a procedure described elsewhere. Corrosion of the test specimens after the TiO^{2+} was added to the acid was insignificant ($K \leq 0.001$ mm/year) during both short (6 hours) and long (up to 500 hours) periods of holding the test specimens in the sulfuric acid solution. It was further found that the concentration of TiO^{2+} could be reduced to 60 mg/l without reducing its effectiveness. The effectiveness of TiO^{2+} as a corrosion inhibitor was thus confirmed. Figures 4, table 1; references 6 (Russian).

UDC 621.794:620.198

Producing Wear-Resistant Coatings on Pump and Accessory Components by Anodization in Supercooled Electrolyte

917M0010 Moscow *KHIMICHESKOYE I NEFTYANOYE MASHINOSTROYENIYE* in Russian, No 9, Sep 90 pp 25-27

[Article by Ye. Ye. Averyanov, candidate of chemical sciences, R. M. Galimzyanov, K. Z. Gilyazova, V. A. Popov, A. V. Rabinovich, and R. A. Shagikhmetov, candidates of technical sciences]

[Abstract] The problem of replacing cast iron pump components with components made of aluminum alloys with a reinforcing coating has become critical in vacuum machine building. In order to develop wear-resistant aluminum-based coatings, the authors of the research reported herein tested processes for chemical nickel plating, chrome plating, applying combined coatings (thin-layer anodization and subsequent spraying of titanium nitride on a Bulat unit), and thick-layer anodization. The first two processes proved to be complicated and little suited to vacuum equipment because of the zinc sublayer formed. Direct application of coatings onto aluminum alloys on a Bulat-type unit also proved to be impossible. The protective coatings produced by the anodization method turned out to be far superior to metal components since they do not distort the component's shape and the cost of anodization proved to be significantly less than that of the electrochemical and chemical methods. Next, the authors developed a unit for anodization in a supercooled electrolyte. It was based on an NSL 250/70 (Hungary) low-temperature laboratory panel, and it permitted the production of temperatures to -60°C in a freezing chamber with the necessary capacity (about 0.5 m³). A 20% sulfuric acid solution was used as the anode. The coatings produced by using the unit developed proved to have satisfactory microhardness, and reliability tests conducted on pump components coated when using the new unit yielded positive

results. Thus, the research conducted showed the feasibility of using anodization in a supercooled electrolyte in cases where protective coatings with high mechanical parameters are required. It was also established that the method developed is suitable for anodizing the covers of mechanical pumps and their accessories. Figures 3; references 3 (Russian).

UDC 628.165:532.71

Preventing Contamination of Membranes by Sediments of Slightly Soluble Compounds

917M0011A Kiev *KHIMIYA I TEKHNLOGIYA VODY* in Russian Vol 12 No 9, Sep 90 (manuscript received 9 Apr 90) pp 811-819

[Article by A. A. Kavitskaya]

[Abstract] The world literature has come to refer to the contamination of membranes by slightly soluble compounds as scaling. Scaling, one of five identified types of sediment formed on membranes, includes contamination caused by the precipitation of such water-soluble salts as CaCO_3 , CaSO_4 , BaSO_4 , SrSO_4 , and CaF_2 . Scaling is generally thought to occur when the product of the activities of the ions included in the make-up of a slightly soluble compound increases the product of that compound's solubility; in other words, desalinated water turns out to be supersaturated with this compound. The authors of this review hypothesize that the contamination of membranes by slightly soluble compounds in reverse-osmosis systems occurs given the following three conditions: achievement of supersaturation in the pressure line of the reverse-osmosis device, the presence of crystallization centers, and an increase in the nucleation centers formed into crystals. Both heterogeneous and homogeneous crystallization take place. Numerous works have examined the mechanism of this membrane contamination. A set of works has also been devoted to developing inhibitors preventing the precipitation of CaCO_3 onto membranes. Another set of works has examined ways of preventing the contamination of membranes by CaSO_4 , BaSO_4 , SrSO_4 , and CaF_2 sediments. Four principal prevention strategies have been discussed in the literature at great length: 1) introducing scaling inhibitors; 2) preventing membrane contamination by reducing the degree to which water is used; 3) preventing contamination in the premembrane treatment stage; and 4) using the method of "nucleation center" reverse osmosis. Figures 3, tables 2; references 55: 16 Russian, 39 Western.

UDC 541.64:678.745(088.8)

Using Polyacrylamide Flocculants To Intensify Cleaning of Electroplating Waste Waters

917M0011A Kiev *KHIMIYA I TEKHNLOGIYA VODY* in Russian Vol 12 No 9, Sep 90 (manuscript received 10 Apr 90) pp 822-825

[Article by V. F. Kurenkov, I. R. Trubina, F. I. Churikov, and V. A. Myagchenkov, Kazan Chemical Technology Institute imeni S. M. Kirov]

[Abstract] Polyacrylamide flocculants are widely used to regulate the stability of natural and industrial dispersions and provide higher-quality removal of suspended particles from waste waters. In an effort to intensify the cleaning of electroplating waste waters, the authors of the study reported herein studied the effect of various characteristics of flocculants and waste waters on the process of sedimentation of a disperse phase. As polyacrylamide flocculants the authors used anionic copolymers of acrylamide with sodium acrylate and cationic copolymers of acrylamide with dimethylaminoethylmethacrylate. The waste waters examined had a pH of 8.7 and an alkalinity between 2.2 and 4.8 mgEq/l and contained the following (mg/l): Ni^{2+} , 12.5-14.0; SO_4^{2-} , 250-490; and Cl^- , 70. The average particle diameter in the disperse phase was $2.3 \cdot 10^{-5}$ m (estimated by the Stokes formula). It was discovered that the flocculating effect increases as the concentration and molecular weight of the copolymer increases and as the content of ionogenic links in the copolymer composition increase. The flocculating effect is a function of the sequence in which the components are introduced, and it intensifies as the concentration of the disperse waste water phase decreases and as the concentration of NaCl increases. The effect was virtually independent of pH level when the pH was between 7 and 10.5. The copolymers of acrylamide with sodium acrylate were the more effective of the two copolymers tested. Figures 5, table 1; references 8: 7 Russian, 1 Western.

UDC 547.292:546:214

Ozone Cleaning of Ammonia-Containing Trap Waters at Nuclear Power Plants

917M0011C Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 12 No 9, Sep 90 (manuscript received 26 Mar 90) pp 825-829

[Article by M. A. Grachok, S. A. Prokudina, and M. I. Shulyatyev, Belorussia State Institute of the National Economy imeni V. V. Kuybyshev, Minsk]

[Abstract] Ammonia is one of the components present in the trap waters at nuclear power plants. When it gets into the ion exchange condensate cleaning assembly, it cuts the ion exchange filters' inter-regeneration cycle short, thus making it difficult to clean the trap waters and extract the radionuclides. The ammonia in trap waters also increases the ammonia concentration of a plant's radioactive wastes from 5-15 to 200-250 g/m³. In an effort to solve the ammonia problem, the authors of the study reported herein examined the process of ozone treatment of ammonia-containing trap waters at the Kursk AES in both model and actual solutions. As research objects they used analytical-grade aqueous ammonia solutions, model solutions of the trap waters at the Kursk AES, and ammonia-containing trap waters entering the chemical plant of the primary loop of the Kursk AES for radwaste treatment. According to their tests, the best results were achieved when the ozone

treatment was conducted at a temperature of 50°C, the ozone-air mixture was fed at a rate of 12.5 l/h, and the pH (after correction with 10 M NaOH) was kept between 10.5 and 11.0. When the ozone was obtained from oxygen, it was possible to increase its concentration in the gas mixture to 0.2 g/l, which sharply increased the rate of ammonia oxidation in water. They thus confirmed that ozone treatment followed by distillation is an effective way of removing the ammonia from ammonia-containing trap waters at the Kursk AES. Figures 4, table 1; references 9: 5 Russian, 4 Western.

UDC 541.18.041.2:628.515

Using Flocculant Compositions To Clean Clayish Particle-Contaminated Waters of Placer Metal Mining Enterprises

917M0011D Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 12 No 9, Sep 90 (manuscript received 11 Apr 90) pp 829-833

[Article by V. I. Lebukhov and G. P. Belozarov, Institute of Mining, Far Eastern Department, USSR Academy of Sciences]

[Abstract] Flocculation sedimentation is one of the most promising methods of cleaning circulating and waste waters containing finely dispersed mineral particles. It is becoming especially important in view of the increased attention being placed on problems of the ecology of the water basin in territories adjacent to industrial facilities. The study reported herein examines the prospects of using flocculant compositions to clean the clayish particle-contaminated waters around placer metal mining enterprises. As their test flocculant the authors chose a combination of an anion-active water-soluble polyacrylamide (molecular mass, $1\text{--}2 \cdot 10^6$ carbon units) and the nonionic flocculant polyoxyethylene (molecular mass, $4 \cdot 10^6$ carbon units). Because simultaneous introduction of the two reagents resulted in an effect with very poor reproducibility, they decided to introduce the polyoxyethylene prior to introducing the polyacrylamide. They further decided that the optimum dose rates for the two reagents were 0.04 mg/g for the polyoxyethylene and 0.1 mg/g for the polyacrylamide and that the procedure was most effective when the polyacrylamide was added at least 15 to 300 seconds after the polyoxyethylene had been added. Besides being effective as cleaning agents, the two flocculants in question are nontoxic. Figures 3, table 1; references 9 (Russian).

UDC 628.543.2

Main Trends and Process Flows in Cleaning Oilfield Waste Water

917M0011E Kiev *KHIMIYA I TEKHOLOGIYA VODY* in Russian Vol 12 No 9, Sep 90 (manuscript received 11 Apr 90) pp 834-837

[Article by D. M. Bril, All-Union Scientific Research Institute for the Collection, Preparation, and Transport of Oil and Petroleum Products, Ufa]

[Abstract] Significant amounts of waste waters are currently being generated in the oil industry, with most being attributed to oil recovery. In view of the vast quantities of water needed to maintain seam pressure during oil recovery, using oilfield waste waters for purposes of maintaining seam pressure is an important engineering and environmental protection measure. The All-Union Scientific Research Institute for the Collection, Preparation, and Transport of Oil and Petroleum Products has developed a combined technology for separation and preliminary dehydration of oil and cleaning of waste waters in a well product collection system. The system is distinguished by the following: 1) breakdown of the stable gas-water-oil mixtures in a collection system by using natural factors and, when necessary, physico-chemical and thermal effects; 2) creation of a system in the system's end sections for preliminary stratification of the broken-down liquid mixtures; 3) removal of the evolved gases and water; and 4) use of differentiated discharge of the free water to reduce the load on the water traps and thus improve the quality of the cleaned water. Other advances by the All-Union Scientific Research Institute for the Collection, Preparation, and Transport of Oil and Petroleum Products include the following: replacement of RVS-type settling tanks with pressure equipment; development of settling tanks with OPF-3000 cartridge filters; and development of sewage treatment processes in which filters containing charges of granular hydrophobic materials and elastic foamed plastic are used in the final stage, thereby resulting in a residual total impurity content not exceeding 10 mg/l. Figures 3, tables 2; references 3 (Russian).

UDC 628.515:66

Protection and Rational Use of Underground Waters of Rubezhnoye Industrial Unit

917M0011F Kiev KHIMIYA I TEKHOLOGIYA
VODY in Russian Vol 12 No 9, Sep 90 (manuscript
received 26 Dec 89) pp 837-839

[Article by A. D. Shelest, N. Ye. Beseda, and Ye. G. Kalugina, Organic Intermediate Products and Dyes Scientific Research Institute, Rubezhnoye Affiliate]

[Abstract] Because the underground waters of the existing artesian well system in the Rubezhnoye industrial unit are the source of domestic and drinking water of a number of enterprises, they were analyzed to determine their sanitary-chemical characteristics. It was found that the waters in question contain amounts of nitro and amino compounds and phenol that exceed the maximum permissible concentrations for water used for domestic and drinking purposes. Of special concern is the fact that the waters move in the direction from the enterprise to the drinking water intake. Because of this, a system to divert this flow of underground waters and use it for the power-generating needs of the local TES is now under construction. It was recommended that the most contaminated of the waters be subjected to cleaning at

the existing biological cleaning and aftertreatment facilities. It was further recommended that the less contaminated waters from the wells located in the western part of the enterprise be used (after stabilization treatment with oxyethylidenediphosphonic acid (OEDP) as a salt deposition inhibitor) in place of river water to replenish the circulating systems supplying water to the association. Finally, it was recommended that OEDP be added (in doses of 5-7 mg/l) to the heat exchange equipment in the water circulation system along with sodium polyphosphate (in a dose of 3-5 mg/l). It is estimated that so doing will provide a 95% level of protection against encrustation of the equipment and a 55% level of protection against corrosion. Tables 3; references 2 (Russian).

UDC 628.543

Tertiary Sewage Treatment

917M0011G Kiev KHIMIYA I TEKHOLOGIYA
VODY in Russian Vol 12 No 9, Sep 90 (manuscript
received 1 Feb 89; after revision 30 May 90) pp 846-849

[Article by A. A. Plysyuk and S. D. Popova, Azot Production Association, Cherkassy]

[Abstract] The economical use of water and protection of water reservoirs against depletion and pollution have become critical. One method of addressing the problem has been to create systems to recycle waste waters by subjecting them to aftertreatment, thus making it possible to use them in place of a portion of the fresh river water used by enterprises. After examining the related literature, the authors of this article propose that final treatment of waste waters intended for recycling be implemented in three stages. In the first stage, the waters are diverted to biological ponds for biological purification. Next, they are directed through aerated filters. In the third and final stage they are subjected to ozone treatment for 15-20 minutes at an ozone dose of 20 mg/l. Tables detailing the waste waters' content of various compounds, oxidability, microbe number, coloricity, pH, and coli titer after each stage in the process are provided. Figure 1, tables 4; references 5: 4 Russian, 1 Western.

UDC 628.322:661.433

Intensifying Disinfection of Water From Spore Forms of Bacteria

917M0011H Kiev KHIMIYA I TEKHOLOGIYA
VODY in Russian Vol 12 No 9, Sep 90 (manuscript
received 28 Feb 90) pp 852-854

[Article by Ye. D. Babenkov, A. I. Borisov, and T. S. Svistunov, All-Union Scientific Research Institute of Railroad Transport and All-Union Scientific Research Institute of Railroad Hygiene, Moscow]

[Abstract] The rate of disinfection of natural water is described by a first-order reaction equation and is generally determined by the resistance of the microorganisms, the physicochemical make-up of the water, and the type and dose of disinfectant. The time for which the water being disinfected and the disinfectant must remain in contact with one another varies with the temperature at which the disinfection process is implemented, with a longer contact time being required in winter. The authors of the study reported herein develop a quantitative estimate of the possibilities of accelerating the disinfection of water by breaking down aggregates of bacteria. They studied the kinetics of chlorine (30-35 mg/l) disinfection of water containing 10^7 - 10^8 spores of *B. cereus* (strain No 96). They conducted tests with and without mechanical agitation in water with a pH of 6.7-6.9 in Moscow at an air temperature of about 13°C. Stirring did accelerate the disinfection process (reducing the duration of the process by a factor of 1.8); however, a significant exposure time (50-70 minutes) was still required. Increasing the intensity of stirring by a factor of approximately 10 did not have a positive effect. Further research did, however, permit the authors to develop a method of intensifying the disinfection of water in a layer of granulated charge. According to their method, the water being disinfected is chlorinated and directed into a column with a granular charge capable of adhering to the spores. This results in intensified mixing of the water and chlorine and increases the time of the spores' actual contact with the disinfectant, thus accelerating the disinfection process. The process developed was recommended for use in the railroad industry's water supply system. Figures 2, tables 1; references 10: 7 Russian, 3 Western.

UDC 628.35

Biological Flocculation of Suspended Substances in Mine Waters

917M00111 Kiev KHIMIYA I TEKHNLOGIYA
VODY in Russian Vol 12 No 9, Sep 90 (manuscript
received 23 Mar 90) pp 855-857

[Article by I. A. Zolotukhin, Yu. A. Petrukhnin, and S. D. Starkov, Perm State Pedagogical Institute]

[Abstract] Biological methods of coagulating and flocculating highly disperse contaminants are superior to chemical methods in that the biological methods are cleaner ecologically, do not require any chemical processes that pollute the environment, and reduce the consumption of nonrenewable resources (oil and gas) needed to produce chemical reagents. In the case of mine waters, which are characterized by a low content of soluble organic contaminants and are incapable of building up the required amount of activated sludge, the task of bioflocculation may be accomplished by using a biomass or photosynthesis products that have been specially isolated from algae. Eight pure algae cultures (four blue-green, three green, and one red) were studied as

possible bioflocculants for purifying mine waters from the Severnaya mine of the Vorkutaugol Production Association. Only one, i.e., *Tolipothrix tenuis* Kutz, promoted an increase in clarification effect. After 30 minutes of settling time, the concentration of suspension in water to which the *Tolipothrix tenuis* Kutz had been added decreased from 340 to 115 mg/dm³ (as opposed to a drop to only 300 mg/dm³ in the control water after free settling for 30 minutes). The experiments thus confirmed that it is, in principle, possible to use algae cultures for biological purification of mine waters. The authors call for further research on the process in a variety of directions, including development of a technology to cultivate the biomass directly in the contaminated mine water on a special carrier. Figures 2; references 6: 5 Russian, 1 Western.

UDC 579.695

Using Immobilized Microorganisms To Clean Phenol-Containing Geothermal Waters

917M0011J Kiev KHIMIYA I TEKHNLOGIYA
VODY in Russian Vol 12 No 9, Sep 90 (manuscript
received 27 Mar 90) pp 857-858

[Article by V. I. Rybnikova and M. I. Zakiyeva]

[Abstract] Bringing geothermal waters into the country's fuel and energy balance has posed a number of priority problems related to developing efficient and ecologically clean methods of cleansing geothermal waters of toxic components, specifically phenols. The authors of the study reported herein compared the cleaning of phenol-containing geothermal waters by using microorganisms immobilized by cleaning and activated sludge at a temperature between 25 and 55°C. The experiments were conducted on a laboratory unit consisting of two sequentially connected columns, i.e., aerator tanks filled with an inert carrier. Geothermal waters with a mineral content of 24.3 g/l containing the following (mg/l) were used as the test waters: phenols, 7.8; calcium, 78.0; magnesium, 40.2; sulfates, 118; iron, 1.6; and chlorides, 12,944. The liquid was aerated by a microcompressor with a capacity of 30 l/h. To obtain a complex of carrier-immobilized destroyer bacteria (the two strains used were *Arthrobacter* sp. T/1 and *Bacillus* sp. T/2), the authors used the airlift method to pump the geothermal waters for 5-7 days at 50°C. No phenol was detected in the water after day 7. In a second experiment to examine the effect of temperature, the authors discovered that the process is more efficient at a water temperature of 26°C than at 50°C; in the first case only 6 hours was required for the immobilized bacteria to completely eliminate the phenols versus 8 to 10 hours at the higher temperature. When activated sludge was used in place of the immobilized microorganisms, the process was slower and less efficient (only a 90% removal of phenols after 8 hours, and phenols were still present after 12-16 hours). Figure 1; references 8 (Russian).

UDC 546.799.5

Selected Hydroxide Compounds of Pentavalent Americium

917M0012A Leningrad *RADIOKHIMIYA* in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received
26 Jan 90) pp 4-6

[Article by I. G. Tananayev]

[Abstract] It is known adding alkalis to neptunium (V) solutions results in the precipitation of a hydroxide residue that, under a layer of mother liquor, slowly transforms into compounds of the type $MNpO_2(OH)_2 \cdot xH_2O$ ($M = Li, Na, K$) and $M_2NpO_2(OH)_3 \cdot xH_2O$ ($M = Na, K$) that can be identified by x-ray phase analysis. The authors of the study reported herein hypothesized that under specified conditions, individual hydroxide compounds of pentavalent americium containing alkaline metal ions in the outer sphere are formed in alkaline media as happens in the case of neptunium (V). Proceeding from this hypothesis, they synthesized a series of hydroxide compounds of pentavalent americium by beginning with a solution containing ^{243}Am with an admixture of 0.1% ^{241}Am . Compounds of the type $MAmO_2(OH)_2 \cdot xH_2O$ were formed in solutions with an $[OH^-]$ level between 0.1 and 0.5 mol/l. As the $[OH^-]$ level increased, compounds of the type $M_2AmO_2(OH)_3 \cdot xH_2O$ were precipitated. The latter compounds were precipitated primarily when the $[OH^-]$ level surpassed 2 mol/l. In the case of $LiOH$, only $LiAmO_2(OH)_2 \cdot xH_2O$ was precipitated regardless of the $[OH^-]$ level. The resultant compounds were confirmed by x-ray phase analysis. From the standpoint of their chemical properties, the compounds synthesized were very stable over time in dry form and under a layer of mother liquor. In both cases, no changes were detected in the compounds after 14 days. Depending on the OH^- concentration and coagulation time, the solutions obtained generally contained between 5 and 10 mg/l more americium than residue. The fact that compounds of americium (V) were indeed produced proved the hypothesis that hydrated ion forms of pentavalent americium $AmO_2(OH)_2^-$ and $AmO_2(OH)_3^{2-}$ are present in alkaline solutions. Tables 5; references 5: 3 Russian, 2 Western.

UDC 539.194:546:79

Electronic Structure and Chemical Bond in Complex $UO_2(NO_3)_2 \cdot 2H_2O$

917M0012B Leningrad *RADIOKHIMIYA* in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received
13 Oct 87) pp 14-18

[Article by M. V. Ryzhkov, V. A. Gubanov, and A. M. Rozen]

[Abstract] Theoretical data about the electronic structure and chemical bonding in complexes, clusters, and solids (which may be obtained through nonempirical single-electron calculations) not only make it possible to interpret extensive experimental materials but also help in

formulating criteria for the directed search for systems with specified properties. For several reasons, the volume of this type of theoretical information related to actinoid compounds is currently very limited. Working within the framework of the relativistic method of discrete variation based on a linear combination of atomic orbitals [LCAO] decomposition of molecular orbitals and a local approximation for volume-correlated potential, the authors studied the uranyl complex $UO_2(NO_3)_2 \cdot 2H_2O$, which is the simplest of a broad series of uranyl groupings with different oxoligands. The data obtained by the relativistic approach were then compared with the results of nonrelativistic calculations for the very same complex. It was found that both the uranyl- NO_3 and the uranyl- H_2O chemical bonding that occur are essentially the result of the interaction of the $U5f$ - and $U6d$ -orbitals with the $O2p$ -shells. This interaction is very important in that it largely determines the charge density distribution of the ligands closest to the uranium, which in turn affects the atoms of the second coordination sphere and onward. The bonds of uranyl with NO_3 and H_2O were found to be comparable with one another. In conclusion, the authors noted that in the complex studied it is hard to find a region where relativistic effects may be ignored. The only area that they deemed apparently suitable for consideration in a non-relativistic approximation was that of the extended organic oxoligands. Figures 2, tables 2; references 9: 6 Russian, 3 Western.

UDC 545.86:546.662:546.659

Stability Constants of Hydrolysis Forms of Plutonium (IV) and Solubility Product of Its Hydroxide

917M0012C Leningrad *RADIOKHIMIYA* in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received 9 Jun 88)
pp 18-25

[Article by E. M. Pazukhin and Ye. G. Kudryavtsev]

[Abstract] The ratio of the stability constants of hydrolysis forms of plutonium (IV) and the solubility product of its hydroxide determines its behavior at different pH values of solutions. These data may be used in the analytical chemistry of plutonium and in forecasting plutonium's behavior when it enters living organisms and when it is buried in geological formations with different make-ups. The study reported herein was undertaken to determine the solubility of plutonium (IV) hydroxide in the range of pH values between 1.5 and 10 and to calculate the stability constant of $Pu^{(IV)}$ and the solubility product of $Pu(OH)_4$. The solubility of product was determined in thermostatted vessels with a volume of 25 ml and at a temperature of 25 plus or minus 1°C. The plutonium concentration was determined radiometrically and, when possible, by weight. The pH level was measured by using a glass electrode that had been precalibrated based on the concentrations of perchloric acid solutions against a background of sodium perchlorate at an overall value of $I = 3$. The experiments were

conducted in three groups with different pH ranges (group 1, pH = 1.5-1.8; group 2, pH = 1.9-2.5; group 3, pH = 2.6-12). The stability constants for the different pH ranges (β_{1-4}) and solubility product [SP] were then obtained by processing resultant data on an Elektronika-60 computer. The estimated values required for the computation were derived by the graphic differentiation method. The following values resulted: $\beta_1 = 3.020 \cdot 10^{12}$; $\beta_2 = 1.900 \cdot 10^{24}$; $\beta_3 = 3.415 \cdot 10^{35}$; $\beta_4 = 2.669 \cdot 10^{46}$; and $SP = 3.675 \cdot 10^{-32}$. The authors concluded the concentration of the neutral form $Pu(OH)_4^0$ is mandatory for a complete description of the system studied. Otherwise unequivocal results cannot be obtained. This was demonstrated by the fact that up to a pH level of 1.8 the solubility of plutonium (IV) hydroxide is equally well described by using the one value β_1 or all the values β_{1-4} . Up to a pH level of 2.5, the system is described by the two stability constants β_1 and β_2 . Up to pH = 2.8, the experimental and calculated results agree only in the case of the case of the three constants β_1 through β_3 . Figures 4, tables 5; references 19: 10 Russian, 9 Western.

UDC 546.799.5+546.799.6+546.799.8

Stability of Tetravalent Curium and Californium Ions in Potassium Phosphorus Tungstate

917M0012D Leningrad RADIOKHIMIYA in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received 4 Sep 89)
pp 36-40

[Article by V. M. Chistyakov, A. A. Baranov, P. N. Karbovnihiy, Ye. A. Yerin, and G. A. Timofeyev]

[Abstract] The production, stabilization, and study of the stability of actinoids in higher valence states, specifically curium and californium, is a serious problem in modern radiochemistry. The authors of the study reported herein studied the stability of curium (IV) and californium (IV) in potassium phosphorus tungstate ($K_{10}P_2W_{17}O_{61}$) solutions in the case of different pH levels, tetravalent metal concentrations, and complexing agents. Isotopically pure ^{249}Cf and a curium preparation consisting of 92.9% ^{248}Cm , 7.1% ^{245}Cm , and 0.03% ^{244}Cm were examined. It was shown that in the solutions used, curium (IV) and californium (IV) are reduced to a trivalent state. The process of the reduction of tetravalent curium and californium ions was found to occur in accordance with two parallel reactions (zero- and first-order reactions, respectively) relative to the concentration of the actinoid's tetravalent ion. The reduction of tetravalent metals in accordance with the zero-order reaction was found to result from the radiolytic processes occurring in the solution, and the first-order reaction was linked to the chemical processes occurring. Under the test conditions, the yield of the reduction of curium (IV) was about twice the yield of the reduction of californium and more than an order of magnitude greater than the yield of the reduction of americium (IV). Experiments studying the reduction of curium (IV) and californium (IV) as a function of the excess $K_{10}P_2W_{17}O_{61}$ revealed that, for both, the effective rate constant increases as the

excess of KPW increases. This was in contrast to the behavior of americium (IV), whose effective rate constant has previously been shown to decrease as the excess of KPW increases. Hence the conclusion that the effect mechanism of the complexing agent ion on the process of the reduction of americium (IV) differs from that in the reduction of curium (IV) and californium (IV). Figures 4, table 1; references 5: 4 Russian, 1 Western.

UDC 542.61

Another Anomaly During Extraction by Diphosphine Dioxides

917M0012E Leningrad RADIOKHIMIYA in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received
18 Dec 89) pp 54-56

[Article by A. M. Rozen]

[Abstract] After analyzing a recently published article by M. K. Chmutova et al., the author of the present article concludes that there is yet another anomaly during extraction by diphosphine dioxides, namely, during the transition from the orthoisomer to the metaisomer of methylphosphorylated benzene, the reagent's basicity decreases while its extraction capability increases. This conclusion as to the existence of a new anomaly is drawn from an analysis of previously published data regarding the extraction of actinoids and nitric acids by diphosphine dioxides (methylphosphoryl-substituted benzenes) with a meta- and ortho-position of the CH_2R_2PO phosphoryl groups. The author speculates that the reason the orthoisomer possesses increased " $HClO_4$ -basicity" is related to the bidentate nature of the reaction of $HClO_4$ with both reagents, whereas americium is coordinated by orthoreagents in a monodentate pattern. He further speculates that the basicity found reflects the contribution of spatial factors and does not reflect the donor capability of the oxygen. It is concluded that IR spectroscopy and research on the reaction of the reagents with customarily used donors (e.g., phenol) could clarify the issue. Table 1; references 9 (Russian).

UDC 542.61

Extraction of Uranium (VI) From Phosphoric and Perchloric Acid Solutions by Neutral Bidentate Organophosphorus Reagents

917M0012F Leningrad RADIOKHIMIYA in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received 8 Jan 90)
pp 56-61

[Article by M. K. Chmutova, M. Yussunua, M. N. Litvina, N. P. Nesterova, B. F. Myasoyedov, and M. I. Kabachnik, Institute of Geochemistry and Analytical Chemistry imeni V. I. Vernadskiy, USSR Academy of Sciences, Institute of Nuclear Physics, France, and Elementoorganic Compounds Institute imeni A. N. Nesmeyanov, USSR Academy of Sciences]

[Abstract] Oxides of diaryl[dialkylcarbamoymethyl]phosphines have been widely studied as extractive reagents for extracting transplutonium and rare earth elements, $U^{(VI)}$, and $Pu^{(IV)}$ from nitric acid solutions and have also been studied with respect to extracting transplutonium and rare earth elements from hydrochloric and perchloric acid solutions. In continuation of this line of research, the authors of the study reported herein attempted to use these reagents to extract uranium (VI) from phosphoric and perchloric acid solutions and their mixtures. Attempts were made to extract uranium (VI) from phosphoric acid by solutions of diphenyl-, ditolyl-, and dibutyl-[diethylcarbamoymethyl]phosphines (Ph_2Et_2 , Tol_2Et_2 , and Bu_2Et_2 , respectively). Neither the oxides of diaryl[dialkylcarbamoymethyl]phosphines nor the dioxides of tetraphenylmethylenediphosphine (even in amounts up to the maximum concentration) resulted in the extraction of uranium from 1- to 8-mol/l solutions of H_3PO_4 . Adding oxides of diaryl[dialkylcarbamoymethyl]phosphines to the given systems was found to result in a synergetic effect that caused the coefficients of the distribution of uranium (VI) to increase by a factor of about 5 to 15 in the case of oxides of diaryl[dialkylcarbamoymethyl]phosphines and by a factor of about 50 for a system with dioxides of tetraphenylmethylenediphosphine. It was further found that oxides of diaryl[dialkylcarbamoymethyl]phosphines were very effective extractive reagents for extracting uranium (VI) from perchloric acid solutions. Adding small amounts of perchloric acid to the phosphoric acid solutions did result in the extraction of uranium (VI). Without this addition, uranium (VI) could not be extracted by either oxides of diaryl[dialkylcarbamoymethyl]phosphines or dioxides of tetraphenylmethylenediphosphine. Figures 5; references 11: 4 Russian, 7 Western.

UDC 546.791

Laser Radiation Intensification of Sorption Processes in Synthetic Ion Exchangers

917M0012G Leningrad RADIOKHIMIYA in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received 24 Jul 89)
pp 83-86

[Article by L. B. Shurmel, T. V. Molchanova, V. V. Rodionov, N. P. Stupin, N. G. Zhukova, and L. I. Vodolazov]

[Abstract] It has previously been shown that the laser method of modifying ion exchangers makes it possible to increase the capacity of commercial ion exchangers without destroying their mechanical strength. It has further been established that laser irradiation helps create a more regular granule structure in ion exchangers, with the absorbed uranium and uranium-containing ions being more evenly distributed throughout the depth of the irradiated granules than throughout nonirradiated granules. The study reported herein examines the process of the sorption of uranium on the anion exchanger VP-1-Ap and the cation exchanger CG-1m under the effect of pulsed CO_2 -laser

radiation on ion exchanges in both uranium-unsaturated and uranium-saturated states and during the sorption process as a function of the degree of dispersion of the ion exchangers' granules. It was determined that in the case of sorption of uranium on the cation exchanger CG-1m with synchronous laser irradiation, the capacity to absorb uranium increases as the granule size decreases. This effect was found to be related to the surface effect of laser activation. The laser irradiation was found to facilitate the sorption of low-charge hydrolyzed or polymerized uranium complexes. In the case of the anion exchanger VP-1Ap, the effect of granule size turned out to be ambiguous since the increase in absorption capacity was found to be related not only to activation of the uranium absorption process itself but also to a change in the ion exchanger's make-up. Figure 1, tables 2; references 5 (Russian).

UDC 502.55(204):621.039.7

Using Fiber Sorbents To Concentrate Radioactive Cesium From Fresh Natural Water

917M0012H Leningrad RADIOKHIMIYA in Russian
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pp 89-92

[Article by A. I. Nikitin, A. I. Kabanov, and L. A. Bovkun]

[Abstract] The method of concentrating radioactive cesium on sorbents based on the fiber complex Mtilon-T (developed at the Moscow Textile Institute) is widely used to control radioactive pollution of sea water in view of its reliability, simplicity, and rapidity. The sharply increasing volume of such clean-up operations after the Chernobyl accident has necessitated the development of an analogous method to control fresh water reservoirs. The study reported herein continues the line of research that led to the development of Mtilon-T, but from the standpoint of concentrating radioactive cesium from fresh water rather than from sea water. Full-scale experiments were conducted to study the sorption of dissolved radioactive cesium from fresh natural waters by using Mtilon-T-based fibers impregnated with copper ferrocyanide. Actual specimens from water reservoirs that had been contaminated during the accident at the Chernobyl Nuclear Power Plant were used. It was found that using a sorbent charge of 0.8 g/cm^2 resulted in the sorption of more than 90% of the ^{137}Cs in the water specimens tested regardless of the rate at which the water flowed through the space filled with the Mtilon-T fiber complex. When the fiber complex was used at a rate of about 1.0 g/cm^2 and when the water flowed through an area of 1 cm^2 filled with sorbent at a specific flow rate of 0.2 l/min , a sorption of at least 95% of the ^{137}Cs in the water was achieved. The experiments conducted confirmed the feasibility of using Mtilon-T fiber complex-based sorbents to extract radioactive cesium from natural fresh waters. Figures 2, tables 3; references 2 (Russian).

UDC 546.791

Development of Standard Specimens for Isotope Dilution Method. II. Standard Specimen With Isotope Ratio $^{233}\text{U}/^{236}\text{U}$ and Uranium Concentration*917M0012I Leningrad RADIOKHIMIYA in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received 3 Sep 89)
pp 99-104*

[Article by M. V. Ryzhinskiy, M. Yu. Vitinskiy, and A. V. Lovtsyus]

[Abstract] In the past few years, researchers involved in analyzing spent nuclear fuel, i.e., in the precision determination of the content and isotope make-up of uranium and plutonium by the isotope dilution method, have focused increasing attention on using the internal standard (or internal calibration or normalization) procedure. This article describes a procedure for manufacturing and certifying a state standard specimen for the make-up of a uranium solution. The starting materials for manufacturing the standard specimen solution were the standard specimen for a ^{233}U solution produced in accordance with State Standard Specimen [GSO] 3213-85 and the state standard specimen for a uranium isotope in the form U_3O_8 diluted in nitric acid and produced in accordance with GSO 4213-87. The solutions were mixed so that the $^{233}\text{U}/^{236}\text{U}$ ratio was about 1 and the concentration of HNO_3 in the solution was about 3 mol/l. Certification of the specimens was performed by using the isotope dilution method of mass spectrometry with an internal standard. In addition, the starting materials used in the standard specimen were sent to laboratories in Austria and France for independent analysis. The authors present an algorithm for calculating analysis results when an internal standard is used. The $^{233}\text{U}/^{236}\text{U}$ molar ratio of the specimen developed amounted to 1.0174 plus or minus 0.0006 with a uranium concentration in the solution of 2.0080 plus or minus 0.0016%. The specimen developed, which was registered under the number GSO 4383-88, was recommended for use when analyzing spent nuclear fuel by the isotope dilution method of mass spectrometry. Figure 1, tables 8; references 6: 4 Russian, 2 Western.

UDC 621.039.626:621.039.54

Accumulation of Americium and Curium in Oxide Fuel of Fast Reactors*917M0012J Leningrad RADIOKHIMIYA in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received 4 Sep 89)
pp 105-107*

[Article by V. I. Borisenkov, A. M. Mitin, A. P. Chetverikov, O. V. Ishunina, N. P. Leontyev, Yu. S. Popov, and G. A. Timofeyev]

[Abstract] Uranium-plutonium oxide fuel is currently the main fuel for fast reactors. Transplutonium elements, which largely determine radiation conditions when the fuel is stored, transported, and processed,

accumulate as the fuel is irradiated. The accumulation of transplutonium elements depends on the isotope make-up of the initial fuel, its americium content, and the irradiation mode and time. In view of these facts, the authors of the study reported herein examined the content of transplutonium elements in fuel with different initial parameters. They studied three fuel elements with different plutonium burn-ups and contents. Two of the fuel elements were irradiated in a BOR-60 reactor, and one was irradiated in a BN-350 reactor. It was discovered that the accumulation of ^{241}Am and ^{242}Cm were linearly dependent on fuel burn-up. When the plutonium content in the fuel elements increases, there is a sharp increase in the accumulation of americium and curium isotopes. Analysis of the results obtained for different cross sections of the fuel element irradiated in the BN-350 shows that no axial migration of americium, curium, or plutonium occurs. However, a comparison of the results of analyzing the cross sections at -480 mm and +480 mm indicates that radial migration does occur. The plutonium content in the cladding is about twice that in the middle, and the contents of ^{241}Am and ^{242}Cm in the cladding are about 3-3.5 times higher than in the center. This anomalous content of ^{241}Am and ^{242}Cm was attributed to the migration of the transplutonium elements themselves and to the migration of the plutonium, which is the source of americium's formation. Figures 3, table 1; references 2: 1 Russian, 1 Western.

UDC 539.1.078.1:539.163

 α -Spectrometric Determination of Isotope Ratios $^{239}\text{Pu}/^{240}\text{Pu}$ and $^{238}\text{Pu}/^{241}\text{Am}$ *917M0012K Leningrad RADIOKHIMIYA in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received
12 Sep 89) pp 109-112*

[Article by S. V. Anichenkov and Yu. S. Popov]

[Abstract] It is accepted that knowing the isotope make-up of plutonium is important in optimizing the accumulation of transplutonium elements and in producing and using nuclear fuel. X-ray fluorescence analysis, mass spectrometry, and high-resolution γ -spectrometry are used to obtain such data. More recently, the method of semiconductor α -spectrometry began to be used for such analysis. In the α -radiation spectra of mixtures of the nuclides ^{239}Pu and ^{240}Pu and mixtures of ^{238}Pu and ^{241}Am , the difference between the energies of the groups of the isotopes' lines amounts to about 10 keV. Hence the strict requirements that have been imposed for sources when the α -spectrometry method is used. The study reported herein demonstrates the possibility of determining the isotope ratios $^{239}\text{Pu}/^{240}\text{Pu}$ and $^{238}\text{Pu}/^{241}\text{Am}$ by using a type DSP series-produced Si(Au)-surface barrier detector with an energy resolution of about 25 keV along the 5486-keV line of ^{241}Am . The α -radiation sources were prepared by the method of evaporation with insulin as described elsewhere. The authors developed a method and program for processing the α -radiation spectra of nuclides on an Elektronika

DZ-28 microcomputer with resolution of the complex peaks into component α -lines. The program is controlled by the BT-128L operating system (developed by the Moscow Chemical Technology Institute imeni D. I. Mendeleev). The authors used their method and program to calculate the branching coefficients of the energy transitions for the nuclides ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Am , and ^{244}Cm . The relative error ranged from 0.7 to 10%, and between 2 and 3 minutes was required to analyze the spectrum of one isotope. The ratios $^{239}\text{Pu}/^{240}\text{Pu}$ and $^{238}\text{Pu}/^{241}\text{Am}$ were also determined. The relative error in determining the activity ratios amounted to about 12% and was due primarily to the selection of the parameters of the model of a single α -line, the statistics of counting the pulses at the peak, and the precision of the energy calibration of the analyzer's scale. The method was recommended for researching the "fine" structure of the α -radiation of individual nuclides. Figures 4, tables 2; references 7: 5 Russian, 2 Western.

UDC 541.15

Contribution of Radiolysis Components of Extractive Reagent Solution to Change in Its Hydrodynamic Characteristics

917M0012L Leningrad *RADIOKHIMIYA* in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received
19 Aug 89) pp 117-119

[Article by A. G. Pribush, V. Ye. Gumenyuk, and G. F. Yegorov]

[Abstract] Irradiation of the extractive reagent solutions used during the extraction refining of irradiated nuclear fuel results in the formation of a broad spectrum of radiolysis products. A portion of these are surfactants. The accumulation of surfactants in turn results in a change in hydrodynamic characteristics, for example, in the rate of stratification of a water-organic emulsion. The stratification time of phases in extraction disperse systems is limited by the aggregation of the emulsion's drops. The hydrodynamic properties of an extractive reagent solution may therefore be characterized by the rate of aggregation of the drops of the disperse phase. In this context, the study reported herein examined the contribution of products of the radiochemical transformations of an organic diluent and tri-n-butyl phosphate to the change in the aggregative stability of an extraction emulsion. The rate of coalescence of the drops of electrolyte in an organic solution of tri-n-butyl phosphate was studied as a function of the irradiation dose to the organic phase. The research objects were two-phase water-organic systems in which the organic phase consisted of n-dodecane and a 30-vol% solution of tri-n-butyl phosphate in n-dodecane and in which the water phase consisted of a 3 mol/dm³ HNO₃ solution or distilled water. It was discovered that the presence of tri-n-butyl phosphate in the irradiated solution does not affect the aggregation rate. It was further shown that it is the carbonyl-containing products of radiolysis of the

diluent that are responsible for the change in the solution's hydrodynamic characteristics. Hence the conclusion that the compounds responsible for the change in the hydrodynamic characteristics of solutions of extractive reagent are formed during radiation transformations of the diluent, with only a small portion of the diphylic radiolysis products possessing surfactant properties. Figures 4, tables 1; references 3 (Russian).

UDC 541.15+546.791+546.799.3+4

Investigation of Kinetics of Reaction of H Atoms With Actinoid Ions in Acid Aqueous Solutions by Pulse Radiolysis Method

917M0012M Leningrad *RADIOKHIMIYA* in Russian
Vol 32 No 4, Jul-Aug 90 (manuscript received
16 Jan 90) pp 123-126

[Article by A. V. Gogolev, V. P. Shilov, A. M. Fedoseyev, and A. K. Pikayev]

[Abstract] A number of works devoted to the radiation chemistry of uranium (VI) and plutonium (III) and (IV) have hypothesized the participation of H atoms in the oxidation or reduction reactions of the specified ions. The study reported herein was undertaken to verify this hypothesis within the framework of a systematic study of the reactivity of the radiolysis products of water with actinoid ions. The authors used the pulse radiolysis method to determine the rate constants of the reactions of an H atom with the ions Pu^(VI), Pu^(IV), Pu^(III), Np^(IV), Np^(III), U^(VI), and U^(IV) in HClO₄ and H₂SO₄ solutions based on the competition of the H atom with benzoic acid, methylene blue, or IrCl₆²⁻. It was discovered that with respect to the series U^(VI), Np^(VI), and Pu^(VI), there is a dependence between the reaction constant (k) and potential of the pairs (E⁰_{(VI)/(V)}). The reaction constants turned out to be an order of magnitude lower in HClO₄ than in H₂SO₄. The reaction of the H atom with Np^(III) and Pu^(III) expands the number of reactions in which the H atom plays the role of an oxidizing agent. Hydrogen atoms were found to react effectively with ions of tri-, tetra-, and hexavalent actinoids, while reduction of an ion of the pentavalent actinoid NpO₂⁺ occurs slowly, if at all. Tables 7; references 7: 3 Russian, 4 Western.

UDC 621.039

Potential Hazard of Solidified Radioactive Wastes

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pp 127-131

[Article by A. S. Barinov, M. I. Ozhovan, I. A. Sobolev, and N. V. Ozhovan]

[Abstract] Most of the radioactive wastes formed as a result of the operation of nuclear power plants are water concentrates of salts that have been classified as wastes with a medium level of activity. Because of their high mobility, these wastes represent a great threat when they

enter the environment. The three most widely used ways of immobilizing these wastes at the present time are to impregnate them with cement, bitumen, and glass. In the study reported herein, full-scale and laboratory tests were conducted on medium-activity radioactive wastes from pressure tube reactors that had been impregnated with each of the three aforementioned substances and then stored under ground surface disposal conditions. The goal of the tests was to develop quantitative conclusions regarding the relative effectiveness of the three materials as means of immobilizing radioactive wastes and thus reducing their threat to the environment. Numerical estimates of the potential hazards of the wastes before and after solidification were made. The possible total losses of radionuclides from the solidified blocks during the time of their storage were also determined. It was discovered that although all three substances provided a good degree stability when the materials were exposed to the action of water, the wastes solidified by impregnation with glass provided the best protection against the leaching of radionuclides into the environment. The glass-impregnated wastes had a leaching factor (cm^2/day) of 10^{-10} versus a factor of 10^{-3} for the cement-impregnated wastes and $5 \cdot 10^{-6}$ for the bitumen-impregnated wastes. It should also be added that despite its relatively high degree of technological complexity, the technique of impregnating medium-activity radioactive waste with glass is economic feasible because of the minimum costs required for transportation and for situating mobile radioactive waste processing stations. Figure 1, tables 2; references 8: 6 Russian, 2 Western.

UDC 541.14:535.37:535.21:536.42

Principles of Controlling Photochemical Reactions in Molecularly Organized Microsystems

917M0013A Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 8, Oct 90 (manuscript received 10 Apr 90) pp 2197-2210

[Article by M. V. Alfimov, Institute of Chemical Physics imeni N. N. Semenov, USSR Academy of Sciences, Moscow]

[Abstract] The problem of the selectivity and effectiveness of chemical reactions is key to a number of scientific

and technical fields. In organic photochemistry, for example, the selectivity of chemical processes determines the size of the yield of the principal reaction product and eliminates the need for laborious purification procedures to remove by-products. In writing this review the authors began from the hypothesis that the photochemical reactions in molecularly organized systems may be controlled on the basis of initiating (by heat or light) phase transformations. Photochemical reactions of arylenes in liquid and solid solutions, hydrosols, and microcrystals were investigated along with the effect of the supermolecular organization of the reagents involved. It was discovered that the laws governing photochemical reactions in liquid and solid solutions, hydrosols, and microcrystals differ. The make-up of photolysis products and the mechanisms and kinetics of photochemical transformations depends on the molecular organization of the reagents. The strongest difference was observed for the amorphous and crystalline states of arylenes. Reagents were found to have a random orientation in the amorphous microparticles of hydrosols. In microcrystals, the reagents' orientation is strictly determined. This finding led the authors to address the problem of controlling the effectiveness and selectivity of the photolysis of arylenes by controlling the phase state of the reaction medium, i.e., by using the crystallization method. They examined the photoinduced crystallization of microdisperse films and hydrosols of cis-isomers of diarylenes (particle size, 1-10 μm). Those amorphous particles with a correct spherical shape were transformed into crystals; at an exposure of 10^{16} photons/ cm^2 , most of the particles were crystallized. The molecules of the trans-isomer were determined to be the initiators of the crystallization. The authors thus demonstrated that it is possible to change the direction of photolysis by light-induced transformation of amorphous microparticles into a crystalline state, with the rate of crystallization depending on the concentration and nature of the photoproduct. Next, in an experiment involving a system of octadecanes and an oil-and-water emulsion, they demonstrated that crystallization of one of the components of an emulsion particle can change the distribution of reagents in a disperse particle in emulsions and accelerate the chemical reactions occurring at the interface. Figures 11; references 12: 7 Russian, 5 Western.